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**RADIATION DAMAGE
FROM INTERNAL ALPHA DECAY IN THORIUM**

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(Ph.D. Thesis)

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ABSTRACT

We have investigated a promising new technique for producing radiation damage in metals by homogeneously doping the metal (in this case thorium) with some short-lived atomic species whose decay produces sufficient radiation damage to permit study by conventional techniques. The relative advantages and disadvantages are discussed.

Radiation damage was accumulated at 4.2°K, and a rough isochronal anneal covering the 4.2-1150°K temperature range was performed. Additional isochronal and isothermal recovery studies were performed in the 4.2-80°K temperature range. The upper boundaries of the various stages are as follows: Stage I (48°K), Stage II (230°K), Stage III (400°K), Stage IV (1100°K). Total Stage I recovery was only 30%. Stage I was found to have five substages with assignments of substage sources being the same as in copper. Long-range interstitial migration in Stage I_E was clearly demonstrated, but distinction between various interstitial models was not possible. Activation energies were determined for the following stages: I_B (0.021 ± 0.002 eV), I_D (0.0875 ± 0.002 eV), I_E (0.0869 ± 0.002 eV), and, subject to assumptions discussed herein, II_A (0.100 ± 0.01 eV) and II_B (0.182 ± 0.01 eV).

I. INTRODUCTION

All crystals in thermodynamic equilibrium at a temperature above zero degrees Kelvin are imperfect in that they contain point defects. The most simple of these structural defects are the vacancy, which is a missing atom in the crystalline array, and the interstitial, which is an atom located in a nonlattice position in the array. The thermodynamic necessity for the existence of these defects has been readily shown by many persons.¹ Other common point defects consist of impurity atoms which may be situated substitutionally or interstitially. The formation of defects such as vacancies and interstitials requires energy; however, the increased configurational entropy resulting from permuting the defects among the various lattice sites produces a net reduction in the total free energy of the crystal. The equilibrium number of defects existing at some temperature is determined by minimizing the free energy. It can thus be readily shown that the atomic fraction of any isolated point defect is given by

$$\frac{n}{n_0} = A e^{-\Delta H_f / kT}, \quad (I-1)$$

where ΔH_f is the formation enthalpy of the defect, n is the number of defects, n_0 is the total number of lattice sites, and A is a pre-exponential factor containing all entropy terms except the configurational one. At atmospheric pressure, however, the $P\Delta V$ term is negligible and ΔH_f can be considered equal to E_f , the formation energy. In similar fashion, groups of point defects (for example, divacancies, trivacancies, etc.) can exist in fractions denoted by equations similar to Eq. (I-1), where allowance is made for the binding energies of the complex and the reduction in the number of permutations associated with a given number of defects as a result of the necessity for treating the defects as pairs, threes, etc. Both theoretical^{2,3,4,5} and indirect experimental^{4,5} work have shown that in most real crystals the agglomerations of defects have significantly higher formation energies than the single defects, inasmuch as the formation energy of the agglomerate is approximately equal to $n_d E_f^i - B$, where n_d is the number of defects in the agglomerate, E_f^i is the single defect formation energy, and B is

the binding energy (in metals, B is typically 0.1-0.6 eV,^{2,3,4,5} compared with typical E_f^* values of 0.6-2.0 eV^{6,7,9,10,11} for vacancies and 3-9 eV^{6,7,9,10,11} for interstitials^{*}). As a result of the exponential dependence of Eq. (I-1) on E_f , the single vacancy is the only thermodynamically stable point defect present in significant quantities at temperatures substantially below the melting point. Thus, other than the dislocations and dislocation complexes that characterize all materials, a typical metal is likely to contain only vacancies and impurity atoms at moderate temperatures. At room temperature and below, the equilibrium concentration of vacancies will range from a few parts in 10^6 to a part in 10^{12} or less, depending upon E_f and the temperature. The amount of time required to achieve the equilibrium value, however, is substantial at low temperatures, so that if a metal is quickly cooled from an elevated temperature to a low temperature, a large excess vacancy concentration can be obtained.

A. Fundamentals of Radiation Damage

Radiation damage in a metal results in the displacement of atoms from their lattice sites, resulting in interstitial-vacancy pairs, also known as Frenkel pairs, the components of which may be close to one another (bound pairs or close-pairs), or they may be separated by a considerable distance, in which case the interstitial is said to be free.

At very low temperatures both interstitials and vacancies will be immobile, since typical vacancy migration energies are about the same as their formation energies (0.6-2.0 eV), while migration energies of interstitials are typically of the order of 0.1 eV in fcc metals.^{8,9} The specific nature of the resultant microscopic radiation damage is dependent upon a variety of factors such as the type, energy and flux of the incident radiation, the material being irradiated, and the temperature at which the irradiation occurs. The essential point about radiation damage is that equal numbers of interstitials and vacancies are produced.

^{*}The activation energy, or potential hill which must be surmounted in order to create an interstitial-vacancy pair (Frenkel pair) is typically of the order of 25 eV; that is, the displacement energy of an atom in a solid is typically of the order of 25 eV or greater (see, for example Ref. 1, p. 66).

Numerous survey articles (for example, Refs. 12, 13, and 14) and several books (for example, Refs. 8, 15, and 16) discuss the general subject of radiation damage and various relationships between the damage and certain physical properties. The basic types of primary damaging radiation are gamma rays (and x rays), electrons (betas), protons, neutrons, deuterons, alpha particles, and fission fragments, in order of increasing mass. In addition, a high energy primary particle can, in turn, displace atoms from the solid in which they are absorbed, and these secondary particles, known as primary knock-ons, can often carry sufficient energy to displace other atoms. These primary knock-ons have the mass of the solid being irradiated. In the laboratory reference system, the maximum amount of energy that can be transferred to a lattice atom in a nonrelativistic collision can easily be shown (by conserving energy and momentum) to be

$$E_2^{\max} = \frac{4m_1 m_2}{(m_1 + m_2)^2} E_1, \quad (I-2)$$

where the subscripts 1 and 2 refer to the projectile and the lattice atom, respectively, and m and E refer to mass and energy. The energy required to displace an atom from its lattice site varies from material to material but is generally in the range from 20-30 eV.^{8,14}

In addition to the effects due to mass differences between the projectile and the in-situ lattice atom, the energy spectrum of the bombarding particle will, in turn, affect strongly the energy spectrum of the primary knock-on. If E_2^0 is the threshold energy for atomic displacement, it can be shown¹⁷ that in the energy range from E_2^0 to $E_2^{\max}$ the energy spectrum of the primary knock-on is inversely proportional to $(E)^2$; that is, the density of knock-ons having energies within any given energy range will be inversely proportional to the squares of their energies. Hence, secondary damage due to the knock-ons will be primarily due to relatively low energy knock-ons whose masses are equal to the masses of the other lattice atoms and which may therefore be expected to efficiently transfer their energy to other neighboring lattice atoms. In the case of electrons that are typically relativistic at energies characteristic of radiation damage studies,

Eq. (I-2) does not apply; however, it can be shown¹⁴ that for relativistic electrons,

$$E_2^{\max} = \frac{2m_1 E_1}{m_2 E_0} (E_1 + 2E_0), \quad (\text{I-3})$$

where E_0 is the electron rest mass energy (0.511 MeV).

Finally, the differential scattering cross section for a charged primary particle (alpha, deuteron, etc.)—for example, Rutherford scattering—can be expressed as

$$\sigma_2 = \frac{4\pi m_1}{m_2} (Z_1 Z_2)^2 \frac{R^2 a_0^2}{E_1 E_2}, \quad (\text{I-4})$$

where Z_1 and Z_2 are the charges of the projectile and target. R is 1 Rydberg (13.6 eV), and a_0 is the Bohr radius. The interesting dependence here is the inverse proportionality to the projectile energy and the knock-on energy. The effect of Eqs. (I-2) through (I-4) on the damage produced in a crystalline material may be summarized by noting that the density of damage will be greatest when the mass of the projectile is highest (since the lattice atom can generally be assumed to be heavier than the radiation). Further, the damage will tend to be highly localized in regions where displacements occur, because the inverse dependence of the scattering cross section on projectile energy and on knock-on energy tends to distribute the energy deposition of the primary radiation over a large distance, whereas the $1/E^2$ dependence of the knock-on spectrum tends to localize secondary damage. A perturbing effect is the phenomenon of focusing collisions, in which an atom at one end of a row is struck and some atom far down the row is ejected from its lattice site. A similar effect is often seen in billiards when a row of billiard balls is struck end-on: all balls remain in place except the last ball, which comes flying off the end. Silsbee,¹⁸ Leibfreid,¹⁹ and Gibson, Goland, Milgram, and Vineyard²⁰ have shown that for low energy transfers (for example, less than 300 eV in copper) appreciable focusing occurs. Experimental evidence by Thompson,²¹ who observed preferential ejection of atoms in prominent crystallographic directions in silver and gold foils, and by Wehner²²

in sputtering experiments tends to verify the role of focusing collisions as a delocalizing mechanism in energy deposition.

As a consequence of the nature of energy deposition from incident radiation, the residual damage resulting from irradiation by light particles such as electrons tends to consist mainly of interstitial-vacancy pairs or of very small clusters of interstitials and vacancies. Neutron damage tends to produce larger clusters of interstitials and vacancies in addition to simple interstitial vacancy pairs. For still heavier particles such as deuterons and alpha particles, the size of the average clusters tends to be relatively larger; however, for a given energy deposition from an alpha particle and a neutron, the neutron will produce more permanent damage than the α particle due to the large amount of ionization produced by the alpha particle. In the case of the heavy particles such as neutrons, deuterons, and alpha particles, there are two regions of interest, generally known as the thermal spike and the displacement spike.¹³ In the thermal spike region the incident particle or the primary knock-on loses energy over a sufficiently large volume that the local temperature does not rise near the melting point. Near the end of the particle path the rate of energy loss per unit distance traveled (dE/dx) becomes very large and the local heating rate far exceeds the ability of the lattice to conduct the heat away. Under these conditions Seitz^{12,13} has calculated that the local temperature far exceeds the melting point of the material. The region in which this localized melting occurs is known as the displacement spike region. Brinkman has estimated that during the time that the material is "molten" self annealing occurs so that upon resolidification a more or less perfect lattice results.¹³

The atoms in the resolidified crystal will not, in general, lie on their original lattice sites; however, the parent lattice should tend to nucleate the recrystallization so that the resolidified displacement spike should be very similar to the original crystal, with the possible exception of a few vacancy clusters and misoriented crystallites with accompanying dislocations and dislocation loops. Any superlattice, however, should be locally disordered. Displacement spikes should be expected near the end of the path (where dE/dx is the greatest) of any heavy particle. Brinkman and Gilbert also note,¹⁷ however, that

because the time during which the crystal will be "molten" will vary with the surface area-to-volume ratio of the molten region when the primary particle energy or the knock-on energy becomes too low, the "molten" state will not exist long enough to permit self-annealing so that I-V pairs will also be produced near the very end of the particle track. Brinkman¹⁷ also estimates this lower energy value. Focusing effects should also contribute to this low energy cutoff for displacement spike formation.

In fission fragment damage, macroscopic voids can be expected to form and fill with the gaseous fission products. Quere²³ notes some evidence of this in the swelling of uranium rods when bombarded by neutrons in the core of a nuclear reactor. Presumably some voids in materials which have been heavily alpha damaged will contain helium gas until such time as the gas diffuses out of the material.

B. Behavior of Defects in Solids

Several different types of interactions between defects and the lattice and between different defects are possible. Groups of vacancies and groups of interstitials can agglomerate to form complexes such as divacancies, trivacancies, diinterstitials, etc. That this is possible can be seen qualitatively in the case of vacancies because the creation of one vacancy requires the breaking of all of the nearest neighbor bonds of one atom (for example, six in fcc materials). Hence two isolated vacancies would represent two sets of broken nearest neighbor bonds, whereas for the case of two adjacent vacancies (that is, a divacancy) you must break one less than two sets of nearest neighbor bonds (in fcc, only 11 bonds must be broken instead of 12). The resultant lowering of the total energy of the system represents the binding energy of the complex. Such an argument as this is of course oversimplified in that it neglects such factors as the strain energy associated with the vacancies due to the relaxation of the lattice; however, it does yield a qualitative understanding of the reasons for the agglomeration of defects. Defects such as interstitials and vacancies can annihilate, thus lowering the lattice free energy. In addition, vacancies and interstitials can be bound to impurities in the lattice, and can even be bound to each other as "close pairs" without

annihilation occurring because the vibrational amplitudes of the atoms may not be sufficiently large at low temperatures to permit the interstitial to jump into the vacant site which the vacancy represents.

The state in which an irradiated material exists will be determined primarily by its temperature-time history during and after irradiation. If n is the number per unit volume of some type of defect, then the annealing rate or the time rate of change of this defect concentration can be written as²⁴

$$\frac{dn}{dt} = -K_0 F(n) e^{-E_m/kT}, \quad (I-5)$$

where $F(n)$ is any continuous function of n , E_m is the defect migration energy, K_0 is a pre-exponential factor which can be shown to be temperature independent, T is the absolute temperature, and k is Boltzmann's constant. The assumptions made in Eq. (I-5) are that the annealing occurs by a single activated process characterized by a constant activation energy independent of n , and that the annealing is independent of the concentration of other defects. If the latter is not true as would be the case where the number of interstitials and the number of vacancies were not approximately equal, and yet neither number was negligible with respect to the other, then K_0 will contain some functional dependence, usually linear, on the concentration of the other type of defect. These assumptions are generally rather unrestrictive. As can be seen from Eq. (I-5) the exponential dependence of the defect concentration on the ratio E_m/kT is such that at sufficiently low temperatures (for example, liquid helium, or in some materials even liquid nitrogen temperatures) all defects will be essentially immobile. In addition to interstitial-vacancy annihilation, other interactions are possible—for example, the combination of two vacancies or two interstitials, the migration of vacancies or interstitials to sinks or traps, etc. In such cases, Eq. (I-5) would apply only to those defects which are free to move.

As has been noted, typical interstitial migration energies in fcc metals are of the order of 0.1 eV or less while vacancy migration energies range from 0.6 to 2 eV. Migration energies for divacancies are usually less than for single vacancies⁸ while di-interstitials migrate with an energy greater than a single interstitial, but less than

a divacancy.⁸ Other processes which have characteristic activation energies are the release of interstitials and vacancies from traps and the dissociation of interstitial complexes and vacancy complexes. Corbett⁸ discusses the various activation energies associated with various phases of the annealing process in a wide variety of radiation damaged materials.

Corbett⁸ and Damask and Dienes¹ discuss a wide variety of techniques for monitoring the radiation damage and the various stages of the annealing process. The most commonly monitored physical property in metals is the electrical resistivity,⁸ or, equivalently, the electrical conductivity. In pure metals the electrical resistivity is increased by the introduction into the lattice of impurities and lattice defects.²⁵ Ideally, the total resistivity of a metal consists of a residual resistivity, which is independent of temperature and is due to the inherent properties of the metal itself, to impurities, and to lattice defects, and a temperature dependent resistivity which is due primarily to electron-phonon scattering. For low defect concentrations, by Matthiessen's rule, the temperature dependent resistivity is independent of the residual resistivity. In very pure materials at very low temperatures the temperature dependent resistivity component decreases as the temperature to the fifth power so that at very low temperatures the only measurable resistivity is the residual resistivity which is highly sensitive* to impurities and lattice defects.²⁶ The standard resistivity technique is to monitor the change in the residual resistivity due to radiation defects. At low defect concentrations one can expect the increase in residual resistivity to be linearly proportional to the defect concentration, since nonlinear interference effects among defects can be neglected.

$$(\Delta\rho)_r = n_1 \Delta\rho_1 + n_2 \Delta\rho_2, \quad (I-6)$$

where $(\Delta\rho)_r$ is the increase in residual resistivity due to defects such as vacancies, etc. $\Delta\rho_1$ and $\Delta\rho_2$ are the resistivity increments due to defects of types one and two of which there are n_1 and n_2 defects. For

*Electrical resistivity measurements commonly are employed to monitor defect concentrations in the range from 10^{-6} to 10^{-3} atomic fraction (Ref. 8, p. 56).

the case of radiation induced defects, of course, the increase in the residual resistivity is simply proportional to the number of defects produced.

Some of the activation energies for certain stages of the annealing process are very low, and therefore annealing of these stages can be expected to occur at very low temperatures. Typically, for irradiation by light particles (electrons), from 30 to 50% of the radiation induced increment in the resistivity is due to close pairs⁸ which have the lowest of all activation energies for recombination. For this reason irradiation is often performed at liquid helium temperatures (4.2°K) in order to assure that all of the radiation damage is retained for study. Selective annealing for known times at known temperatures, followed by repeated monitoring of the radiation induced increment in the residual resistivity as measured at 4.2°K, provides a means of determining the activation energies characteristic of the various annealing stages. This type of analysis is discussed in detail in Section V. From this information a determination of the type and extent of the damage produced by irradiation is often possible. Extensive radiation damage studies have been performed on such materials as copper, silver, and gold as well as on certain semiconductor materials.²⁷

It might be noted at this point that the requirement of maintaining the irradiated samples at or very near 4.2°K (or even lower for some studies involving gold) imposes severe experimental difficulties due to the problem of having to place the irradiated samples in a vacuum in order to permit irradiation. The problem of maintaining the low temperatures, especially in view of the heating caused by energy deposition from the irradiating beam is not easily solved, especially in materials having relatively low thermal conductivity. These problems are in addition to the expense of, complexity of, and lack of ready access to, the accelerator itself. An alternative which avoids the above problems will be discussed in Section II.

C. Radiation Damage in Fissionable Materials

Since the advent of nuclear reactors there has been interest in radiation damage in fissionable materials. Some of this work has been

reported directly in open literature, especially in the case of uranium, whereas for the other materials such as thorium and plutonium much of the work was initially reported in the classified literature, and although some of this material was subsequently declassified, it has not been readily available as would be the case had the work been initially reported in the appropriate technical journals. Most of the experimental radiation damage work on fissionable materials has been of an engineering nature, being concerned with such features as hardness, fuel element swelling and cracking, etc. Billington and Crawford²⁸ have reviewed thoroughly most of the work on uranium while Corbett²⁹ has reviewed the purely scientific work on uranium. Queré³⁰ has done about the only electrical resistivity studies on radiation damaged uranium; and like most other work on fissionable materials, it was performed on neutron irradiated samples where the gross effects of fission fragment damage tend to obscure the analysis. Queré observed saturation effects in the residual resistivity of his samples. As noted by Corbett,²⁹ theoretical work on point defects in uranium is quite limited, consisting mainly of work by Brailsford,³¹ who predicted an increase in the electrical resistivity of 71 micro-ohm-cm for 1 at.% (atomic percent) interstitials and 28 micro-ohm-cm for 1 at.% vacancies.

Self irradiation studies of the alpha decay of ^{239}Pu have been made by Olsen et al.³² Vineyard is quoted by Olsen et al.³² as having predicted that a total of 1800 interstitial-vacancy pairs would be created for each 5.1 MeV alpha decay—800 pairs by the alpha particle and 1000 pairs by the recoiling ^{235}U nucleus. Olsen determined the number of pairs per decay from the initial $d\rho/dt$ (approximately 0.06 micro-ohm-cm per hour) by Lucasson and Walker's rule.³³ Olsen et al.'s value was 1760 pairs per disintegration. Stored energy measurements³⁴ tend to confirm this value within a factor of 2. Contrasting evidence by Lee et al.^{34,35,36} indicates low temperature anomalies in the initial value of $d\rho/dt$ vs T . While the evidence is not decisive, Lee et al. postulate that these anomalies are due to magnetic phenomena, that is, that Pu is magnetically ordered, such that the radiation damage creates spin disorder as well as lattice disorder. Thus, the change in residual resistivity with damage would appear to

be more sensitive to temperature than would be the case without magnetic ordering since thermally induced spin disorder may be a significant portion of the residual resistivity even at low temperature. For this reason, each defect may have an abnormally large effect upon the increase in residual resistivity so that the application of Lucasson and Walker's rule may not be justified.

D. Summary of Prominent Physical, Mechanical, Metallurgical, Chemical, and Radioactive Properties of Thorium

The basic physical, metallurgical, and chemical properties of thorium, as well as some of the industrial and engineering applications, are rather thoroughly covered in certain survey books.^{37,38,39} Among the basic physical properties of interest are the following. Thorium metal has a melting point of $1690^{\circ}\text{C} \pm 10^{\circ}$. It has a face-centered cubic structure (α phase) up to 1365°C at which temperature it undergoes a transition to a body-centered structure (β phase). The recrystallization temperature lies in the range from 500 – 700°C . (Ref. 37, p. 223). At room temperature the electrical resistivity of very pure thorium is 13–14 micro-ohm-cm.³⁹ The pure metal is relatively soft and quite ductile, and newly annealed thorium resembles lead, both in color and in general mechanical properties. Chemically thorium metal is quite reactive, having an electropositive character similar to that of magnesium. It can exhibit valences of 2, 3, or 4, with 4 being predominant. In particular, thorium forms the highly stable refractory oxide thoria (ThO_2). Thorium also forms numerous compounds with hydrogen, carbon, nitrogen, and the halides, as well as such compounds as sulphates and nitrates. Of particular interest is the compound $\text{Th}(\text{NO}_3)_4$ in aqueous solution because of its role in providing the means to alloy the stable ^{232}Th with very small amounts of the radioactively unstable ^{228}Th .⁴⁰

The interesting nuclear properties of thorium center about the isotopes ^{232}Th and ^{228}Th . ^{232}Th , the naturally occurring isotope, is quite stable, having a half life of 1.42×10^{10} yr for alpha decay whereas the alpha decay half life for ^{228}Th is only 1.9 yr. The decay scheme for ^{228}Th and ^{232}Th are shown in Fig. 1⁴¹ along with the branching ratios expressed in percentages, the alpha energies in MeV

Fig. 1. Decay scheme for ^{232}Th and ^{228}Th .

and the prominent x-ray energies in keV in cases where alpha decays initially leave excited nuclei. A summary of the decay and the average* alpha energy associated with this decay are given in Table 1.

Table 1. Average α energies in thorium decay.

Process	Average α Energy	$T_{1/2}$
1) $^{232}\text{Th} \rightarrow ^{228}\text{Th}$	$\alpha_{\text{avg}} = 3.98 \text{ MeV}$	$1.42 \times 10^{10} \text{ y}$
2) $^{228}\text{Th} \rightarrow ^{224}\text{Ra}$	$\alpha_{\text{avg}} = 5.39 \text{ MeV}$	1.91y
3) $^{224}\text{Ra} \rightarrow ^{220}\text{Rn}$	$\alpha_{\text{avg}} = 5.67 \text{ MeV}$	3.64d
4) $^{220}\text{Rn} \rightarrow ^{216}\text{Po}$	$\alpha_{\text{avg}} = 6.28 \text{ MeV}$	51.5 s
5) $^{216}\text{Po} \rightarrow ^{212}\text{Pb}$	$\alpha_{\text{avg}} = 6.77 \text{ MeV}$	0.16s
$^{212}\text{Pb} \rightarrow ^{212}\text{Bi}$	No α	
$^{212}\text{Bi} \rightarrow ^{212}\text{Tl} \rightarrow ^{208}\text{Pb}$ branch	$\alpha_{\text{avg}} = 6.06 \text{ MeV}$ (branching ratio = 0.36)	
$^{212}\text{Bi} \rightarrow ^{212}\text{Po} \rightarrow ^{208}\text{Pb}$ branch	$\alpha_{\text{avg}} = 8.78 \text{ MeV}$ (branching ratio = 0.64)	
6) $^{212}\text{Bi} \rightarrow ^{208}\text{Pb}$ avg	$\alpha_{\text{avg}} = 7.80 \text{ MeV}$	60.5 m
Average of 2) through 6)	$\alpha_{\text{avg}}^{\text{T}} = 6.38 \text{ MeV}$	

In comparison with ^{228}Th , the number of ^{232}Th decays is completely negligible, even for concentrations of one part in 10^6 of ^{228}Th in ^{232}Th because the ^{232}Th half-life is about 10^{10} times that of ^{228}Th .

As can be seen from Fig. 1 and Table 1, the ^{228}Th daughters have very short half-lives so that once equilibrium is achieved, each ^{228}Th decay can be thought of as producing five alpha particles with a mean energy of 6.38 MeV. Based upon the previously discussed prediction of Vineyard as quoted by Olsen³² and the latter's experience in plutonium for 5.1 MeV alphas, we might expect one 6.38 MeV alpha and the associated recoil to produce approximately $(6.38/5.1) \times 1760$ (Olsen) to 1800 (Vineyard) or 2100-2250 Frankel pairs per alpha decay. In view of the very gross nature of the calculation an approximate figure of 2000

* In those cases where branches exist in the decay scheme so that more than one alpha energy can be considered as characteristic of the decay, an average alpha energy was computed by weighting the alpha energy associated with each branch by the branching ratio.

interstitial-vacancy pairs per alpha decay appears reasonable. Hence, the five alphas associated with each ^{228}Th decay have the potential of creating approximately 10,000 Frenkel pairs, neglecting the self-annealing effects of subsequent alpha decays on previously created pairs.

Recent interest in thorium has been the result of its potential for use as a breeder of the fissionable ^{233}U in reactor fuel elements via the reaction:

This reaction is analogous to the formation of ^{239}Pu from ^{238}U via the reaction:

^{232}Th has been utilized in conjunction with ^{235}U as a reactor fuel material.⁴² In view of the observed tendency of uranium fuel elements to swell^{23,30} and possibly split the cladding which protects the fuel from the corrosive action of the coolant water, a fundamental knowledge of fission fragment damage in fissionable materials is desirable. Unfortunately fission fragment damage on an atomic scale is so great that monitoring some physical property such as the electrical resistivity, which is highly sensitive to the damage, is not likely to yield data which readily lends itself to any straightforward analysis in terms of interstitial-vacancy pairs, etc. An added complication would be the fact that alpha decays would constantly be occurring in the fissionable material and it would be desirable to be able to separate the alpha effects from the fission effects. For this reason we decided to study self damage in some fissionable type material. The reasons for selecting thorium in preference to uranium and plutonium were several. In the case of plutonium, a nearly sufficient reason would be that it is an extremely toxic material and therefore would represent an extreme health hazard. Furthermore, plutonium exists in many different phases with the transition temperatures lying in such a range that the desired isothermal or isochronal anneals involved in the analysis of the damage would result in changes in the crystal structure

which would obscure the effects of the damage itself. In the case of uranium a little work has been done, as mentioned, by Quéré.^{23,29,30} The principal problem with uranium is that pure uranium has an orthorhombic structure. The vast majority of resistivity work on radiation damage has been done on face-centered cubic (fcc) or body-centered cubic (bcc) structures, with the greatest portion of this work having been performed on fcc materials—especially copper. In view of the considerable damage anticipated from alpha decay it would be desirable to be able to compare the results of alpha damage in the fissionable material with the results of the less extreme neutron and electron damage in extensively studied metals such as copper, gold, silver, or platinum (fcc).

Thorium has an fcc structure up to 1365°C and is therefore a desirable material for study. In addition, Albrecht and Himmel⁴³ have done self-diffusion studies in thorium and have found the activation energy for self-diffusion (equal to the sum of the formation and migration energies of single vacancies) of α -Th, the fcc form, to be 77.2 kcal/mole (3.3 eV/atom), and of β -Th (bcc) to be 83 ± 7 kcal/mole (3.6 ± 0.3 eV/atom). A rule of thumb for estimating the formation energy for vacancies in metals is that E_f will be about 1 eV per 1000°C of the melting point. This approximation is generally valid to within 10%. Based upon this rule, then, $E_f = 1.7$ eV in α -Th and thus $E_m = 1.6$ eV. Another desirable feature of thorium is that it is possible to heat it to about 1365°C, a sizeable fraction of the melting point of 1690°C, without inducing a phase change so that quenching experiments, to determine directly the vacancy formation energy for comparison with the work of Albrecht and Himmel, may be possible.

Numerous Atomic Energy Commission reports have been written on various properties and fabrication techniques involving thorium and thorium alloys. In addition to survey books such as Refs. 37-39, specific reports of some interest to the current work are the report of Saller et al.⁴⁴ on cold drawing of thorium wire, the report by Stanley et al.⁴⁵ on fabrication techniques such as

rolling, swaging and extruding of thorium, and the report by Beach et al.⁴⁶ on the electroplating of metals on thorium. Saller et al. and Stanley et al. mention the tendency of thorium metal to stick in dies during wiredrawing and extrusion processes. Saller et al. describe the exotic lubricants devised to permit cold drawing of thorium wire and both Saller et al. and Stanley et al. mention the forming of wire by cladding the wire in a copper jacket which serves as a lubricant to prevent seizing. Both Saller et al. and Beach et al. mention the formation of a brittle Cu-Th alloy at the interface following the electroplating of Cu onto Th. This brittle interface renders electroplated Th unsuitable for wiredrawing. Stanley et al. have noted that while hot rolled thorium can be rolled to thin foils without difficulty, cold rolled foils develop edge cracks after reduction of about 25%. Edge trimming, however, will permit reductions of up to 98% without annealing.

Kittel et al.⁴⁷ have studied the extent to which fission fragment damage induced swelling in Th-U alloys with various amounts of uranium. The fuel elements were formed by various methods including swaging and casting. No study of resistivity versus damage was performed, and annealing effects were examined only through isothermal irradiations at high temperatures. Swelling effects were most severe at high temperatures and high uranium concentrations.

E. Previous Radiation Damage Studies of Thorium

There have been only two experiments in which the resistivity of radiation damaged thorium has been monitored. Bowman et al.⁴⁸ studied in a limited way both the damage and annealing effects of a thorium foil exposed to 38 MeV alpha particles and 19 MeV deuterons from a cyclotron. Brinkman and Gilbert¹⁷ studied 9 MeV proton damage and 18 MeV deuteron and deuteron induced fission fragment damage in thorium.

Brinkman and Gilbert¹⁷ measured the resistivity at -180°C (93°K) and maintained their sample at a temperature between -143°C and -149°C during irradiation. They observed a saturation effect in the resistivity after 9 MeV proton bombardment. They found that the increases in the residual resistivity obeyed an empirical equation:

$$\rho = \rho_0 + a(1 - e^{-t/b})_{-180^{\circ}\text{C}} \quad (\text{I-9})$$

where:

ρ = resistivity in micro-ohm-cm

ρ_0 = initial residual resistivity (5.90 micro-ohm-cm)

a = 3.06 micro-ohm-cm

t = bombardment in particles/cm²

b = 0.475×10^{18} particles/cm².

Hence, Brinkman and Gilbert find a saturation resistivity ratio,

$$(\rho_s/\rho_0) = 1.52 \left(\text{i.e., } \frac{5.90 + 3.06}{5.90} \right).$$

In their experiment they saturated the resistivity by proton bombardment and then began deuteron bombardment, expecting the fission fragment damage to produce some additional annealing of the I-V pairs resulting from the proton damage so that the saturation value of I-V pairs should be less for deuteron induced damage than for proton induced damage. The deuteron irradiation did produce a reduction in the saturation value of the resistivity with the data being fitted by the empirical exponential relation

$$\rho = \rho_{\text{end proton}} + x(1 - e^{-t/y})_{-180^{\circ}\text{C}} \quad (\text{I-10})$$

electrical resistivity of a 6.7 mil thorium foil after periods of 19 MeV deuteron irradiation at temperatures "below -100°C ."⁴⁸ Resistivity measurements were taken at -146°C . They then conducted limited annealing studies at temperatures up to 100°C . A saturation of the resistivity was observed which was analogous to that observed by Brinkman and Gilbert; however, the value of $(\rho_s/\rho_0)_{-146^{\circ}\text{C}}$ of Bowman et al. was 1.30 as contrasted with 1.52 as measured at -180°C by Brinkman and Gilbert. This agreement appears to be fairly good in view of the fact that the irradiation by Bowman was apparently performed at a higher temperature, viz., "below -100°C "⁴⁸ as contrasted to the range -143 to -140°C for Brinkman and Gilbert which would admit the possibility of increased thermal annealing during irradiation. Bowman determined that the resistance ratios at saturation at 300°C and 500°C , respectively, are $(\rho_s/\rho_0)_{300^{\circ}\text{C}} = 1.08$ and $(\rho_s/\rho_0)_{500^{\circ}\text{C}} = 1.06$ and following full annealing the equilibrium value of $(\rho/\rho_0)_{300^{\circ}\text{C}} = 1.03$. Bowman et al. also measured $(\rho/\rho_0)_{-146^{\circ}\text{C}}$ following a 5-min anneal at 100°C and found that $(\rho/\rho_0)_{-146^{\circ}\text{C}} \approx 1.14$.

Bowman et al. measured the thermal conductivity of thorium following the deuteron irradiation and determined that, within experimental error, the Wiedemann-Franz ratio was obeyed.

It should be pointed out, however, that the considerable experience with fcc materials such as copper, gold, and silver indicates that complete annealing of close I-V pairs and long range interstitial migration (at least in the single interstitial model) should be complete at temperatures well below -100°C to -149°C . In addition several other annealing processes whose sources are less well established may be occurring at temperatures below those at which Brinkman and Gilbert¹⁷ and Bowman et al.⁴⁸ performed their irradiations. For this reason an irradiation of a sample held at liquid helium temperature during the irradiation process would be desirable.

A general summary of work on the physical, mechanical, and irradiation properties of thorium and thorium alloys is contained in Ref. 49.

II. SCOPE AND GOALS OF THIS INVESTIGATION

There were two principal objectives in this investigation. These were: first, an attempt to develop an alternative to the standard experimental technique of radiation damage production; and, second, to survey in a somewhat gross fashion the recovery of radiation damage in high purity (99.9+%) thorium over a temperature range of approximately 1000°K and to study in some detail the low temperature structure of the annealing process—that is, to study in some detail Stage I* recovery in thorium.

As was noted briefly in Section I-B, there are numerous experimental difficulties associated with conventional irradiation techniques which involve the use of some sort of particle accelerator. In addition to these problems is the problem of obtaining the necessary time on an appropriate accelerator. This is especially true in situations such as are found in some smaller graduate schools where an appropriate accelerator simply may not be available. Even where accelerator facilities do exist, the expense of performing an experiment involving the accelerator can be substantial. It was decided to attempt to perform a radiation damage experiment where the sample to be damaged would be self-damaging since this obviates the accelerator. Unfortunately very few materials of interest have sufficiently short half-lives, if indeed they are unstable at all. The alternative to having an unstable source material is to dope the source material to be studied with some other radioactive material, having an appropriate decay scheme in concentrations sufficient to produce the desired defect increment or value of $\Delta\rho$ in a convenient time scale. The next problem is the selection of the doping material. If the particles emitted as a

* As has been noted in the many references on radiation damage (for example, Ref. 8), the division of the annealing into various stages is somewhat arbitrary as is the assignment of the mechanisms of some of the substages within the major divisions; however, an attempt has been made to use the same criteria as has been employed with copper.

result of the nuclear decay are charged particles rather than neutrons, gammas, or x rays, then the doping material must be homogeneously mixed with the material to be studied in order to assure uniform damage. In order to do this one must either disperse the dopant uniformly on the surface of the samples and diffuse it in until homogeneity is achieved at the desired concentration of dopant, or one must add the dopant to the molten bulk material. In both cases care must be taken to assure that an unacceptable impurity concentration does not obtain from the doping procedure, and one must ascertain that the dopant is, in fact, uniformly dispersed. The details of the sample preparation are given in Section III, but in summary, it was found that it is possible to add sufficient dopant (~ 1 ppm by number) without introducing impurities, by doping the melts. Homogeneity was obtained through a combination of mechanical mixing in solid form and successive melts. The basic techniques are applicable to a variety of source materials and dopants. The only real drawbacks of these techniques are: first, the concentrated dopant material must often be handled with great care or in a glove box due to its activity; and second, one cannot ever turn off this "accelerator" so it is necessary to correct all data for the fact that damage occurs continuously throughout the experiment. Many of the advantages of having a self-contained damage source are obvious; for example, precise temperature control is not complicated by heating produced by the beam, and isothermal irradiations may be performed in place of isothermal anneals when desired. This can eliminate the need for storing large amounts of damage prior to the annealing operations. Other advantages become apparent after having worked with both means of damage production.

The specific material to be investigated was thorium metal, which as noted is another of the fcc metals. The residual resistivity was to be monitored as a measure of the damage. In addition to the relatively stable ^{232}Th (half life = 10^{10} yr), thorium has a short-lived isotope ^{228}Th which has a 1.9 yr half-life and the ^{228}Th was to be employed as the dopant material. Two doped samples with the dopant concentration varying by a factor of approximately 5 were to be used together with an undoped standard or reference sample. After determining the proper concentration of ^{228}Th and preparing and

annealing the samples the intent was to accumulate a large amount of damage relative to the amount of additional damage which could be expected to occur during the course of data acquisition. A rough isochronal anneal^{*} involving temperature steps of approximately 10-20% of the temperature of the previous annealing point would then be performed in the temperature range from 4.2°K to approximately 1000°K. After determining, on the basis of this rough isochronal anneal, the upper temperature limit of Stage I, two more isochronal anneals would be performed with temperature steps of approximately 2 degrees. The second of these isochronal anneals would be essentially a repeat of the first in order to provide a check on the repeatability of the data and on the compensation procedure which corrects for the continuous damage. The intent was then to perform a pair of isothermal anneals of damage accumulated at 4.2°K in each of the substages detected in the 2 degree isochronals. These isothermals would be performed at identical temperatures but with the difference that in one case an excess of vacancies (radiation predoping) would be introduced by not annealing out the damage which was stable at temperatures up to the maximum of Stage I. This should enhance the annealing rate in any substage which represents the long range migration of interstitials to vacancies. If such a substage could be found this procedure would help to identify clearly this particular substage as being caused by long range interstitial migration, since other processes commonly occurring in Stage I would be unaffected, and this enhanced annealing rate would supplement the inconclusive results of a determination of the substage source based solely upon the reaction order.[†]

The activation energy associated with free interstitial migration is of considerable interest for comparison with other fcc materials whereas the various activation energies for the annealing of the close pairs are of somewhat less interest because in the case of the alpha

^{*}An isochronal anneal is one in which the samples are heated to progressively higher temperatures and annealed for a fixed length of time at each temperature. Following each annealing pulse the samples are cooled to 4.2°K to permit a measurement of the change in the resistivity.

[†]In Eq. (1-5), $F(n)$ is often written as n^γ as will be discussed in Section V. γ is known as the reaction order and can be indicative of the type of process involved in the annealing.

damage involved here there will be several types of close-pair or correlated recovery which may overlap in energy making any meaningful separation quite difficult. From the isochronals and the isothermals it should be possible to determine both the activation energy and the reaction order of each substage.

III. SAMPLE PREPARATION AND MOUNTING

A. Sample Preparation

The samples used consisted of thin (0.002 in. to 0.0025 in.) foils of ^{232}Th homogeneously doped with ^{228}Th to levels of approximately 0.6 and 3.0 ppm (parts per million). The doping levels were selected such that the 3 ppm sample would produce an estimated increase of approximately 1% in the base resistivity of the sample in 10 days of irradiation in liquid helium. This determination was made based upon resistivity increases observed by Brinkman and Gilbert¹⁷ who performed their irradiation at a temperature (-146°C) which was above the anticipated Stage I of the annealing process. Hence they neglected an estimated 50% of the total resistivity increase. Under the assumption that 1 at.% of Frenkel pairs corresponds to an increase of roughly $40\ \mu\Omega\text{-cm}^*$ and with the assumption of 2000 pairs per ^{228}Th decay a doping level of 3 ppm was selected. Preliminary measurements of an undoped sample indicated the ability to measure the base resistivity to at least one part in 10^5 , that is, to 1/1000 of the anticipated 1% increase in resistivity. The time scale of several days was selected so that the damage rate would be slow with respect to the time scale of the annealing schedule. The shape and dimensions of the samples are shown in Fig. 2. In addition to the two doped samples, an undoped reference sample or standard was prepared from the pure ^{232}Th . The ^{232}Th metal used in this experiment was specially prepared by the Ames Laboratory at Iowa State University. The thorium was produced

*This value of $40\ \mu\Omega\text{-cm}$ was arrived at by assuming that the saturation value of the increased residual resistivity represented approximately 1 at.%. The observed increase in $\Delta\rho$ reported in Ref. 17 then corresponded to approximately $40\ \mu\Omega\text{-cm}$ which is in line with Brailsford's³¹ estimates for uranium.

Fig. 2. Sample configuration.

by the iodide process and was then zone refined; it is believed to be some of the purest bulk thorium available anywhere. Table 2 contains an analysis of impurities in the thorium. The ^{228}Th was obtained in 25 mCi amounts from the Radiochemical Centre, Amersham, Buckinghamshire, England, as crystalline ^{228}Th nitrate on ^{232}Th carrier. The total mass of a 25 mCi source of ^{228}Th and ^{232}Th carrier in nitrate form was about 130 μg .

To prepare the samples the crystalline nitrate was dissolved 5 ml of distilled water to which a trace of concentrated nitric acid had been added. It was found to be necessary to add this trace of nitric acid in order to dissolve the crystals. This was perhaps due to the necessity of etching away some protective surface coating on the crystals.

The samples of ^{232}Th which were to be doped were cut from 0.004 in. foils so that the undoped samples were approximately square and weighed from 1.07 to 1.22 g. These samples were folded into the shape of a cup, and the proper amounts of aqueous thorium nitrate solution were pipetted onto the surface of the samples. The water was driven off under an infrared lamp, leaving behind the desired amounts of the crystalline nitrate. The samples were then folded in such a manner as to fully enclose all the nitrate. Heating thorium nitrate to a few hundred degrees centigrade in a vacuum decomposes the nitrate leaving behind metallic ^{228}Th and giving off various oxides of nitrogen as gases. After decomposing the nitrates, the samples were further heated to 1500°C for 45 min in order to diffuse the ^{228}Th into the ^{232}Th foil. The self-diffusion data for Albrecht and Himmel⁴³ indicated that 45 min at 1500°C would be twice the time required to diffuse a thorium atom a distance equal to the thickness of the ^{232}Th foil. In addition, preliminary experiments with trace amounts of ^{228}Th nitrate indicated that indeed the ^{228}Th would diffuse into the bulk ^{232}Th foil. Autoradiographic prints of the surface of doped samples indicated, however, that neither the evaporation process nor the simple diffusion process produced anything approximating a uniform distribution of ^{228}Th in ^{232}Th . The evaporation process produced gross inhomogeneities in distribution and autoradiographic studies of the surface after diffusion indicated very little surface spreading prior

Table 2. Radiochemical Analysis of Thorium Ingot and Test Sample.

Impurity	Concentrations, ppm by weight	
	Ingot	Sample
Fe	575	10
Si	350	35
V	350	ND, <1
Al	<35	<35
B	10	<1
Ni	6	10
Zr	3	10
Cu	3	3
Mg	<1	1
Zn	ND, <5 ^a	ND, <3
Pb	ND, <2	≤6
Ca	<10	<10
Ti	<1	<1
Mn	1	<1
Co	ND, <1	ND, <1
Mo	1	ND, <1
Sr	ND, <1	ND, <1
Na	ND, <100	ND, <100
As	ND, <35	ND, <35
Sb	ND, <10	ND, <10
Cd	ND, <3	ND, <3
Sn	ND, <3	ND, <3
Ba, Be, Cr, Nb	ND, <1	ND, <1
H ₂	—	3, 4 ^b
O ₂	—	761 ^b
N ₂	—	345 ^b
C	—	1000 ^b

^a"ND" means "not detected."^bAtomic fraction (ppm), not by weight.

to diffusion into the bulk. Hence, the doping was homogeneous only in thickness, and not laterally. In view of the difficulty of distributing a fixed amount of the dopant material uniformly over the surface it was decided to melt the ^{232}Th in order to get mixing with the ^{228}Th . This was done in an electron beam melter for 1 min. The preliminary step of heating in the vacuum furnace was continued, however, so as to allow control over the process of nitrate decomposition and to assure that any loss of material due to electron induced sputtering or to surface evaporation while in the molten state would result in the loss of only small amounts of the ^{228}Th since after diffusion the ^{228}Th would be dispersed in the bulk rather than all located on the surface where it might be susceptible to preferential evaporation or sputtering.

After melting, the samples were cold-rolled in a hand mill until edgecracking indicated that annealing was necessary before further rolling. At this point another autoradiograph showed that the ^{228}Th was still not quite uniformly dispersed. The samples were therefore rolled into a ball, remelted for another minute, and rerolled. This time autoradiography indicated an essentially uniform distribution.

Another annealing process (45 min at 1000°C) followed by further cold-rolling produced $3/8$ in. by $4-1/2$ in. foils of some $0.002-0.0025$ in. thickness.

An attempt was made to draw thorium into 0.003 in. wires, but thorium tends to stick in dies and is very difficult to draw so it was decided that foil samples would be easier to make.

The final step of the sample preparation process consisted of placing a teflon mask in the shape of Fig. 2 over the foil and etching away the unwanted material with concentrated hydrochloric acid. Sample uniformity in the 0.056 in. wide gage portion of the sample was found to be very good and it was possible to resistance heat the samples to temperatures up to 1500°C with temperature variations of $\pm 1^{\circ}\text{C}$ across the width of the sample and $\pm 2^{\circ}\text{C}$ along the length of the gage portion. These observations were made in the apparatus described in Ref. 50, the essential components of which were an infrared microscope and a phase-locked detection loop.

It was necessary to perform all rolling and etching operations in a glove box because it was found that micron sized pieces of the doped

foils tended to flake off of the samples in handling. Dow Corning silicon mold release was found to be an excellent lubricant for the rolling operation. The amount of thorium contained in the ThCl_4 which resulted from the etching operation also constituted a health hazard and thus had to be carefully contained.

Immediately prior to the start of the first experimental radiation damage run all samples were resistively heated to about 900°C for 20 min inside the cryostat. This served to anneal out all of the radiation damage which had occurred during handling. Further annealing at 900°C produced no further reduction in the residual resistivity of the sample.

An examination of Table 2 shows that the principal impurities in the thorium ingot obtained from Ames were iron, silicon, and vanadium. After melting these impurity concentrations were greatly reduced, indicating that they perhaps vaporized. Of the nonmetallic impurities, O_2 and N_2 , the O_2 was probably on the surface as was the N_2 since neither is soluble to this degree in thorium. The sample used in this test was rolled using kerosene as a lubricant. Presumably the carbon came from this lubricant. This sample had a resistivity ratio of only 5:1 between 300°K and 4.2°K . Later samples rolled using the silicon mold release were cleaned more carefully and showed a resistivity ratio of 19:1. The final samples were not analyzed for non-metallic impurities because this analysis was performed in a facility which could not risk even slight contamination from trace amounts of ^{228}Th . In view of the increased resistivity ratio some reduction in the carbon content must have been achieved. Thus, it has been demonstrated that the doping process need not introduce more than at most a few parts per million impurities, and with care even this may be reduced.

B. Sample Mounting

The sample holder was constructed entirely from quartz to minimize thermal expansion problems. This sample holder and its mounting arrangement are shown in Fig. 3. The cryostat itself is discussed in Section IV-A. The quartz flange mates to a stainless steel flange which is in turn attached to a 29 in. long hollow stainless steel tube

Fig. 3. Cryostat and sample-holder assembly.

containing six ceramic tubes clustered around a 0.190 in. stainless steel rod and all held in place by teflon spacers. Each ceramic tube has two holes through it to permit the passage of the requisite electrical leads with the ceramic providing the necessary insulation at all temperatures from 1°K to 900°K.

As can be seen from Fig. 3 there are provisions for mounting up to three samples simultaneously—one reference standard and two doped specimens. All samples were wired in series for current so that the same measuring current or annealing current would flow through each sample. Each of the three samples had two 0.004 in. tantalum potential leads spot-welded to it. These leads were attached approximately 1/2 in. on either side of the midpoint of the gage portion of the sample. Tantalum was selected for several reasons. First, it is one of the few pure metals which forms no low melting point eutectic composition with thorium. Most pure metals form eutectics with thorium which melt at temperatures near the anticipated annealing temperature. Secondly, of the otherwise pure metals, tantalum had the lowest thermal conductivity. Third, tantalum could be readily spot-welded to thorium. Fourth, and last, all of the common alloys such as stainless steel contain elements which either form low melting eutectics or brittle eutectics with thorium.

In addition to the potential leads, the reference standard had a platinum vs platinum-10% rhodium thermocouple attached to it at a position midway between the potential lead attachment point and the end of the gage portion of the sample, and a constantin vs "normal" silver thermocouple attached to one of the wide ends of the reference standard.

The samples were clamped at the ends between two 0.150 in. by 0.150 in. by 0.010 in. pieces of OFHC copper held together by two No. 0 stainless steel nuts and a No. 0 stainless steel bolt which passed through the center of the copper squares and the end of the sample. The current leads were pinched between a third copper piece and one of the two copper pieces holding the sample. The current leads themselves passed around the quartz mounting strips, and the stiffness of the current leads helped support the small weight of the samples. The interconnecting current leads on the sample holder were 0.100 in. wide

by 0.010 in. thick OFHC copper strips; the annealing current lead coming into the cryostat was the 0.190 in. diam stainless steel rod. The common return lead was the stainless steel tube containing the ceramic tubes and the stainless steel rod. Stainless steel was selected in order to minimize the heat leak into the cryostat.

IV. EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus consisted of two major components: the cryostat and the resistance bridge. These two components are described separately below.

A. The Cryostat

The basic cryostat is essentially the same as that described in Ref. 51. The only significant differences between the cryostat in Ref. 51 and the one employed here and schematically shown in Fig. 3 are that the top and bottom of the outer can are 0.060 in. thick here instead of 0.030 in. and the cryostat employed here has no stainless steel jacket around the windings of the heater coil. The sample holder containing the samples can be inserted or withdrawn from the inner can. The heating element is a 450 W dc heater which is wrapped around the inner can and which can be used to maintain the samples at any desired temperature between 4.2°K and 850°K while the exterior of the outer copper can is immersed in liquid helium. The walls of the inner copper can are 0.345 in. thick and the bottom is 0.250 in. thick. Both the inner and the outer can are made of OFHC copper. The temperature of the inner can is measured by interchangeable thermocouples which are inserted in stainless steel tubes which connect to holes drilled on opposite sides of the inner can. The thermocouples employed may be gold-2.1 at.% cobalt vs copper, copper vs constantin, or platinum vs platinum-10% rhodium depending upon the temperature range involved. In addition a calibrated germanium resistor may be used for precise temperature determination near liquid helium temperatures; however, the germanium standard may not be used in a radiation environment. A Leeds and Northrup proportional temperature controller feeding a magnetic amplifier connected to the heater coil provided temperature

regulation to $\pm 0.2^\circ\text{C}$. The control signal was supplied by the thermocouple and the thermocouple output was bucked by a zero suppression unit so that the control signal was always between 0 and 1.0 mV. Thus the temperature of the inner can could be precisely controlled. Under normal operation a helium exchange gas would thermally connect the sample with the walls of the inner can; however, separate vacuum systems provided the capability of evacuating independently or simultaneously the inner can, the outer can, and the thermocouple tubes. As noted in the discussion of the sample mounting arrangement a pair of thermocouples attached to the reference sample and useful over different temperature ranges, were available to assure that the inner can and the sample were, indeed, at the same temperature.

The cryostat was originally designed to permit long term isothermal irradiations; hence the massive inner can. It was later found, however, that due to the details of the sample mounting arrangement and the abnormally high temperature coefficient of resistivity, that at temperatures above about $5\text{--}6^\circ\text{K}$ the three samples fluctuated in temperature by about 0.1°K and that the temperature of all three samples varied independently of one another. The resultant resistivity fluctuations precluded the possibility of isothermal irradiations with continuous monitoring of the resistivity and forced the cooling of the entire assembly to 4.2°K prior to each measurement of the resistivity. Operated in this mode, the cryostat was highly inefficient in terms of liquid helium consumption.

The vacuum systems consisted of two Welch Duo-Seal mechanical pumps pumping homemade U-tube liquid nitrogen cold traps. One pump was used as the forepump for a Consolidated Vacuum Corporation (CVC) MCF-300 oil diffusion pump* on top of which was a CVC water-cooled baffle with Thermionics Laboratory's Model RALNT 02SP liquid nitrogen cold trap. The cold trap was isolated from the cryostat by Vacuum Research Company VRC-2TI-EP air operated gate valve with Viton-A O-rings. The second Welch Duo-Seal mechanical pump was available

* Here and elsewhere in this dissertation, reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

for system roughing and for pumping on the liquid helium in the event that temperatures down to about 1°K were desired.

The entire cryostat, as shown in Fig. 3, was suspended in a glass double-dewar with a sealed outer dewar and an inner dewar having a vacuum pumpout to permit pumping out any helium which might diffuse through the glass walls. An excellent high vacuum within the walls of the inner glass dewar is achievable with this type of system by roughing out, back-filling two or three times with high purity nitrogen, each time roughing out the N_2 . After filling the outer dewar with liquid nitrogen and the inner dewar with liquid helium, the remaining N_2 within the walls of the inner dewar freezes out and a hard vacuum is obtained.

As a result of the care taken to minimize heat leaks, it was found that a helium fill every 12 hr was sufficient to maintain the samples at liquid helium temperatures except on those occasions where excessive helium evaporation was caused by supplying large amounts of heat to the heater coil during operations such as high temperature annealing.

B. The Resistance Bridge

The resistance bridge employed here was designed by David Lai of the Lawrence Radiation Laboratory and was constructed on an intermittent basis by a number of persons including the author over a period of several years. The system is capable of measuring voltages as low as 10^{-8} V dc. A components list for the bridge is as follows:

1. Honeywell potentiometer, model 2768 (10^{-8} V sensitivity).
2. Honeywell potentiometer, model 3802 (10^{-7} V sensitivity).
3. Keithly Nullmeter, Model 147.
4. Keithly Nanovoltmeter, Model 148.
5. Electronics Measurements Corp. Regatron Programmable dc Power Supply (0-36 A, 0-40 V dc).
6. Princeton Applied Research Corp. model TC-100.2R high precision constant voltage/current supply.
7. Instrulab, Inc., Evenvolt supply for 1.5 V, 6 V, and 22.5 V supplies to potentiometer.
8. Four Eppley Laboratory, Inc., saturated cadmium standard cells.

9. Leeds and Northrup Standard Resistors: 10 Ω (1), 100 Ω (2), 1000 Ω (1), 10000 Ω (1).
10. Temperature controlled oil bath for standard resistors.
11. 240 A-hr backup storage battery supply for maintaining constant temperature in Evenvolts and standard cells.
12. Trickle-charger for maintaining storage batteries.
13. Four Ohmite 312-3-T2, 30 A, 300 V switches for high current circuit.
14. One Ohmite 312-4-T2, 30 A, 300 V switch for high current circuit.
15. Three Leeds and Northrup thermocouple switches for function selector switches.
16. Four Commander Dual Contact Copper Switches—0.01 μ V thermal emf, 100 $\mu\Omega$ contact resistance; three of which were single brush, 2-pole, 4-position switches; one of which was a single brush, 2-pole, 3-position switch.
17. Massive 32 section OFHC copper terminal block.

The bridge was designed with the intent of maximizing its versatility. It can accept inputs from as many as seven samples. A precisely controlled heating current of up to 40 A at up to 36 V dc can be fed to any of four samples. A constant low current of from 1×10^{-6} A to 0.2 A at from 0-100 V dc can be provided to all seven samples for measuring purposes. The Princeton Applied Research constant voltage/constant current power supply is operated in the constant voltage mode and is set to maintain a constant voltage across a 100 Ω standard resistor which is kept in a temperature controlled oil bath. When employed in this mode the Princeton power supply supplied current varied only a total of three ppm over a period of 4 mo. The sample selected may be placed either in series with one selected standard resistor (10 Ω , 100 Ω , 1000 Ω , or 10000 Ω) for measuring purposes, or when the supply of very low, well regulated measuring currents is desired, it may be placed in series with one standard resistor and in parallel with the other three resistors, the four of which constitute the arms of a current divider network. Figure 4 shows the current supply circuit for four (A, B, C, and D) of the seven samples. The same circuit

Fig. 4. Circuit diagram of current supply and resistance bridge.

also applies to the other three samples except that the high current supply is not available to these samples.

The simplified circuit for measuring the potential drop across the sample(s) and the current through the sample is shown in Fig. 5. As shown in Fig. 5, the potential drop across the standard resistor and across the sample are measured by different potentiometers in the bridge. This is not necessary, since switching is available to permit all measurements to be made on one potentiometer; however, this two potentiometer mode was selected for ease of operation since the resistance readings changed only slightly over short periods of time and the two potentiometer mode required very little dial changing during the course of successive measurements. The two potentiometers were standardized against one another by measuring the emf of a reference standard cell on each potentiometer.

With reference to the nomenclature of Fig. 5 the resistance of the sample can be determined as follows:

$$V_R = I_m R_R \quad (\text{IV-1})$$

$$V_S = I_m R_S \quad (\text{IV-2})$$

Thus,

$$R_S = R_R \left(\frac{V_S}{V_R} \right) \quad (\text{IV-3})$$

Once the resistance of the sample is known, its resistivity can be computed from the standard relationship

$$\rho = R(A/L), \quad (\text{IV-4})$$

where ρ is the resistivity, A is the cross-sectional area of the sample, and L is the distance between the attachment points of the potential measuring leads.

All potential lead pairs running from the cryostat to the bridge were routed through aluminum conduit and the terminal block where the potential leads connect the bridge consisted of massive blocks of OFHC copper, shielded from air currents. These precautions were taken to minimize thermal emfs. Additional precautions to minimize thermal emfs within the bridge include use of low thermal emf solder,

Fig. 5. Potential-measurement circuit.

special low thermal emf switches, careful routing of leads, and elimination of air currents. Oversized, annealed, strain-free copper current leads were employed in the current section. All potential lead pairs were twisted and electrostatically shielded to prevent ac pickup. The entire potentiometer galvanometer system was floated above ground and then a single, high quality ground was provided to prevent ground loop problems. Thermal emf's within the bridge were found to be approximately 20 nV.

The bridge itself contains a total of five standard cells: one internal standard contained within the model 2768 potentiometer and four additional standards in the form of a temperature controlled external standard source box made by Eppley Laboratories. One standard is wired to each of the two potentiometers; one is the reference standard used to cross-check the two potentiometers, and one is wired directly to the terminal block where it is available for external use if necessary.

C. Measurement of Damage Production and Recovery

Prior to the start of each data run the samples were annealed resistively at a temperature of 1100-1200°K for 20 min by passing a current of 3.0 A dc through them; the samples were connected in series. During the annealing operation the sample chamber was evacuated to 3×10^{-6} Torr or lower. A platinum vs platinum-10% rhodium thermocouple was attached to the undoped standard and its temperature was measured; however, no high temperature thermocouples were attached to the undoped standards. The thickness of the doped samples and the standard were not quite the same so the specific resistance of the three samples was not the same and therefore a given annealing current resulted in different annealing temperatures for all three samples. The resistance of the samples was measured at temperature using a Hewlett Packard Model 3560B digital voltmeter and the approximate temperature of the doped samples was determined by scaling the measured temperature in °C of the control sample by the ratio $(R_s^T/R_s^0)/(R_c^T/R_c^0)$ where the subscripts "s" and "c" refer to doped sample and control sample respectively, and the superscripts "T" and "0" refer to the annealing temperature and 0°C respectively. Uncertainties in the absolute value of the annealing temperature were approximately $\pm 30^\circ\text{C}$,

but the annealing temperature itself, as determined above, was repeatable to $\pm 5^\circ\text{C}$. To assure that the annealing temperature did indeed anneal all existing damage, the total annealing time was increased to 40 min prior to the first run with no further reduction in the measured value of the sample resistances. In subsequent runs the starting point following the annealing operation was repeatable to within -1, +7 parts in 10^5 (that is, within -1, +7 by 10^{-8} volts). The measurement capability of the resistivity bridge was $\pm 1 \times 10^{-8}$ V as determined by the repeatability of readings of the resistance of the control sample.

The measuring current used throughout the experiment was 0.1 A in order to obtain five significant figures in measuring the sample resistances. A few preliminary measurements were also made at 0.05 and 0.01 A with no detectable change in the measured resistance of the control standard so all further measurements were made using 0.1 A. As mentioned in the discussion of the resistivity bridge, the Princeton Applied Research regulated power supply was extremely stable, varying in output by only a total of three parts in 10^6 over a period of months. There were several periods of 1 or 2 wk where the maximum fluctuations were less than one part in 10^6 peak to peak. Due to geometrical problems the actual sample resistivities were only estimated (approximately $12 \times 10^{-6} \Omega\text{-cm}$ at room temperature with a resistivity ratio of 19:1 between room temperature and 4.2°K). The incremental radiation damage was always expressed as $\Delta R/R_0$ when R_0 was the value of the resistance following annealing. All measurements of sample resistance were made by averaging the voltage readings obtained with the measuring current flowing in each of the two possible directions. The purpose of this was to cancel out the Seebeck voltages (thermocouple effect) or thermals generated in the potential leads due to the temperature gradients through which these leads run. As can be seen from Eq. (IV-5) the above procedure does indeed cancel out the thermal emf's

$$\begin{aligned}
 E_f &= IR + E_t \\
 E_r &= IR - E_t \\
 \hline
 E_f + E_r &= 2 IR,
 \end{aligned}
 \tag{IV-5}$$

where:

E_f = potential difference measured with measuring current
flowing in the forward direction

E_r = potential difference measured with measuring current
flowing in the reverse direction

I = constant measuring current

R = sample resistance

E_t = thermal emf.

During the damage accumulation period the samples were stored at 4.2°K by surrounding the cryostat with liquid helium and maintaining approximately 1/4 atm of helium in both the sample chamber (inner can) and the buffer (outer can). The damage rate (ΔR vs time) was carefully monitored throughout the storage period since it would be necessary to correct the data taken during the annealing operation for the amount of additional damage introduced during the course of the annealing operation itself. The correction procedure is described in Section V.

In obtaining the isochronal and isothermal data, the buffer was initially evacuated to a pressure of less than 2×10^{-5} Torr. The heater was then turned on and the power level was adjusted so as to be sufficiently high to permit a rapid rate of temperature rise. The maximum power available to the heater was 450 W. Below 40°K it was possible to reliably go from 4.2°K to the control temperature in a matter of a few seconds. For temperatures above 40°K warmup times were 10-30 sec. Upon reaching a point approximately 1 degree below the intended control point all power was shut off to permit the cryostat to coast up to, and stop at the desired control point. As soon as the control point was reached the Speedomax H temperature controller was switched on and a power divider network was adjusted such that the controller could put out a sizeable fraction of 500 W at all times, while the heater in the cryostat would receive only that fraction necessary to maintain the temperature. In other words, the temperature controller worked best when it was trying to control at a power level of approximately 200-400 W. The power divider could be set to feed any desired constant fraction of the controller output to the heater. Thus, as the controller varied its output power by some fraction, the power to the

heater would vary by the same fraction but the absolute power increment would be scaled by the power divider. Temperature control was generally within $\pm 0.1^\circ\text{C}$. The temperature read was determined from the output of the same thermocouple which provided the control signal to the temperature controller (see Section IV-D for details of temperature measurement).

At the conclusion of the annealing pulse, approximately $1/4$ atm of helium exchange gas was admitted to the buffer in order to couple the inner can thermally to the liquid helium bath. With practice, temperature-time profiles approximating a square wave could be achieved. Upon return to 4.2°K the sample resistances were measured. After repeated cycling to temperatures above 50°K short term thermal emfs of from 0.1 - 0.3×10^{-6} V were created in addition to slowly varying thermal emf's of approximately 0.6×10^{-6} V. The slowly varying emf's could be canceled out by the procedure discussed above; however, it was necessary to take several sets of readings in order to average out the short term fluctuations. Under these conditions the scatter in the data increased from $\pm 1 \times 10^{-8}$ V to as much as $\pm 5 \times 10^{-8}$ V. All data with the exception of the four 15 min isochronal points above 500°K were obtained in this fashion. Cycle times ranged from 20 min per point at low temperatures to 3 hr per point above 350°K . The four data points above 500°K were obtained by resistive heating with the temperature estimated as described in conjunction with the discussion of the preliminary annealing process. The reasons for this were threefold. First, the cycle time was becoming prohibitively long and was introducing errors in data due to difficulties in making the proper time correction. Second, in order to cool down rapidly so as to minimize the time correction errors liquid helium was used, and the helium consumption for runs near 500°K approached 35 liters per data point. Finally, at elevated temperatures some outgassing occurred in the system and slight oxidation of the samples was observed, as evidenced by a permanent increase in resistance of the control sample. In the resistive heating mode, however, the walls of the inner can remained cold and there was no outgassing. Cycle times in the resistive heating mode were from 20 to 25 min.

The experimental procedure for the isothermal annealing runs was virtually identical to the procedure employed during the isochronal runs. The only difference was that whereas the isochronal runs consisted of annealing for fixed periods of time at successively higher temperatures the isothermal runs involved a continual annealing at the same temperature with interruptions during which the samples were cooled to 4.2°K to measure the change in the resistivity that had resulted from annealing at that particular temperature for the given period of time. Hence, the isothermal anneals followed the time history of the annealing process at some temperature whereas the isochronal anneals follow the temperature dependence of the annealing.

D. Temperature Measurement

In any experiment where the temperature is an important parameter, considerable care must be taken to assure its proper measurement. The system for temperature control was described in the previous section. As shown in Fig. 3, there were two thermocouple tubes which permitted any desired thermocouple to be inserted or removed at any time. Thermocouples employed in this investigation were gold-3.1 at.% cobalt vs copper, copper vs constantin, and platinum vs platinum-10% rhodium. The gold-cobalt thermocouple was used at temperatures from 4.2 to 300°K; the copper-constantin thermocouple was used from 77-500°K; and the platinum-rhodium thermocouple was used from 300-500°K. The highest temperature to which the cryostat can was heated was 500°K. Whenever possible two thermocouples were used and compared with each other. All thermocouples except the gold-cobalt thermocouple were calibrated by the Lawrence Radiation Laboratory's standards laboratory. The gold-cobalt thermocouple was calibrated by immersing it in liquid helium at 4.2°K and applying a constant percentage correction, based upon the 4.2°K reading, to the National Bureau of Standards tables of the thermal power relative to 0°K. Extensive work by Richard Van Konynenberg⁵¹ employing a germanium standard resistor verified the fact that a linear correction procedure such as that described above is quite valid. This calibration was then cross-checked against the copper-constantin thermocouple and the two were found to be in exact

agreement. Care was taken never to heat the gold-cobalt thermocouple above 300°K since at temperatures of about 310°K and above gold-cobalt thermocouples often change calibration drastically.

As was mentioned in Section III-B there was platinum vs platinum-10% rhodium thermocouple attached to the control standard and a "normal" silver vs constantin thermocouple attached to one of the copper mounting washers of this same control sample. These could not be calibrated in the conventional manner due to the fragility of the assembled sample holder assembly. Their output, however, was measured at room temperature (25°C) and the readings were found to be in agreement with standard tables so no correction was made to readings obtained from these thermocouples.

In order to assure that the samples were at the same temperature as the inner can which contained the other thermocouples, the temperatures measured by the thermocouples mounted on the control standard were compared to the readings obtained from the thermocouples inserted in the thermocouple tubes and there was consistent agreement. No thermocouples capable of reading temperatures below 75°K were mounted on the samples because this type of thermocouple would be ruined by temperatures above 310°K and therefore would not survive the first high temperature anneal prior to the first data run. In view of the large thermal mass of the inner can, the very small thermal mass of the samples, the approximately 1/4 atm of helium exchange gas which was maintained at all temperatures, and the absence of any discrepancy between the readings of the thermocouples located in the can and on the samples, at all temperatures where such comparisons were possible, it has been assumed that the sample temperatures were always the same as the temperature of the inner can, even at very low temperatures. This admits the possibility of deviations of a few tenths of a degree at 4.2° although this is not considered likely. At higher temperatures (5.5-6°K and above) where the inner can is heated, the samples should be at a temperature within 0.1°K of the can temperature.

V. TREATMENT OF DATA

As has been previously mentioned, the damage production and recovery were followed by measuring the increase and decrease of the sample resistance. The assumption here is that the measured increase or decrease in resistance is directly proportional to the number of defects. Implicit in this assumption are the further assumptions that

1. the incremental resistivity per defect pair is independent of orientation of the pair with respect to the electric field direction, and
2. that changes in the resistivity within some recovery stage or substage involves only one recovery process.

In general the first of these is not a good assumption while the second is reasonably good. For lack of any better theory, however, the direct proportionality of the resistivity increment to the concentration of some particular type of defect must be assumed.

The greatest amount of the processing of this data was associated with the correction for the damage which occurred between the beginning of a data run and the time at which some particular data point was taken. This correction was necessitated by the fact that the radiation damage source could not be turned off after accumulating the damage necessary for a given run. In acquiring the data, the time at which each data point was obtained was recorded to permit later correction for this effect.

During the storage period in which damage was accumulated a constant record of the damage rate was compiled for each sample. This did not prove to be strictly linear as is usually the case in light particle damage studies. Recent work by Dworschak et al.⁵² has analyzed the curvature in a graph of $d\Delta\rho/d\phi$ vs $\Delta\rho$ where $\Delta\rho$ is the increased resistivity and ϕ is the time integrated radiation flux. In order to properly correct for increased resistance as a function of time, the resistance-vs-time data was fitted to the expression

$$\Delta R = \phi/\alpha (1 - e^{-\alpha t}), \quad (V-1)$$

which is the integrated form of

$$\frac{d\Delta n}{dt} \approx \frac{d\Delta R}{dt} = \phi - \alpha \Delta R, \quad (V-2)$$

where:

ΔR = increase in resistance

Δn = increase in number of defects

ϕ = resistance increment per unit time produced by the radiation flux

α = fraction of resistance per unit time which spontaneously anneals.

The form of Eq. (V-2) is not exactly correct since the radiation annealing due to spontaneous recombination or localized thermal effects probably varies with the type of defect itself, but Eq. (V-2) will then give some average value of α . The data could be fitted with a standard deviation which was approximately 5% of the fitted values for ϕ and α . Data for different runs were fit with slightly different values of ϕ and α ; however, all values were well within the standard deviation as the total spread of values of ϕ and α was approximately 2%. Equation (V-1) was used to extrapolate $\Delta R(t)$ to the times at which the actual isochronal and isothermal data points were measured.

In analyzing the annealing data, all processed data was expressed as a percentage of the total damage which had been accumulated at the time the data point was taken. The normalization factor was the total amount of damage which would have been present at the time the given data point was recorded. Thus, the normalization factor would be $\Delta R(t)$ where $\Delta R(t)$ is given by Eq. (V-1). The actual amount of damage remaining was $R_m - R_B$ where R_B is equal to the intrinsic sample resistance (as measured immediately after the high temperature anneal), and R_m is the measured value of the resistance at the time the data was recorded. Equation (V-3) expresses in the most simple form the fractional recovery, R_f , which is equal to 1 minus the fraction of the damage remaining, in terms of R_m , R_B , and ΔR :

$$R_f = 1 - \frac{R_m - R_B}{\Delta R}. \quad (V-3)$$

As it stands Eq. (V-3) is valid for the case where no time correction is necessary. As discussed above, however, what is actually desired is the appropriate value of R_m , R_B , and ΔR at some later

time t . If we substitute the appropriate expression for $\Delta R(t)$ based upon Eq. (V-1) we are then left with R_m and R_B . The measured value of R_m represents an actual value of the resistance at the time of measurement, and R_B represents the value of R_m that will ultimately be attained at the time when all annealing is completed. What is desired here is compensation for that amount of extra damage which is still stable at the annealing temperature and which has occurred since the commencement of the run at time t . If t_r is defined as the time at which the first data point for a run was taken, then the stable portion of the extra damage is simply given by $\Delta R(t) - \Delta R(t_r)$ multiplied by the fraction of the damage which is stable at the given temperature. The normalization constant is still $\Delta R(t)$. This last term may be viewed as a subtraction of this extra damage from the measured value of R_m . The end result of this discussion is the expression given in (V-4):

$$R_f = 1 - \frac{R_m - R_B}{\Delta R(t)} + (1 - R_f) \frac{\Delta R(t) - \Delta R(t_r)}{\Delta R(t)} . \quad (V-4)$$

It is to be observed that Eq. (V-4) has not been solved explicitly for R_f , although this would be possible. In practice, Eq. (V-4) is solved by iteration on the computer since $\Delta R(t)$ must be generated initially and an iterative solution provides, as the zero order approximation, the value of the first two terms of Eq. (V-4). The convergence is very rapid (approximately three cycles gives R_f to six significant figures which is better than the quality of the data and is therefore quite sufficient).

The principal source of error in the time correction procedure lies in the neglect of the further additional damage which occurs during the time required to cool down from the annealing temperature. The time correction of R_m is based upon the third term in Eq. (V-4). The scaling factor for the extra damage is $1 - R_f$. From the time that the samples start cooling down until their resistance is read the extra resistance increment will be larger than that given by the numerator of the third term in Eq. (V-4) due to the fact that at lower temperatures a greater fraction of the total amount of extra damage will be stable and thus will require compensation in order to obtain the

correct value of R_m . In other words, the scaling factor is still $(1 - R_f)$, but $R_f = R_f(T)$. In principle a correction could be made by integrating under the time vs temperature cool down curve. In practice this is difficult to do and has been neglected. This omission is generally negligible at lower temperatures where R_f is relatively low and the cool down time very short relative to the total elapsed time prior to the start of the cool down. In the case of the anneals at room temperature and above, however, this error was estimated at approximately 0.4%.

For these higher temperature points a linear approximation was made to the cool down curve and an additional rough correction term was determined. Estimates of the magnitude of this error for 75°K data points taken during the 10 min isochronals indicated that the error was slightly less than 0.1% total recovery. Since the scatter in the data was estimated at approximately 0.1% or greater no additional corrections were made to any data except the higher temperature data from the 15 min isochronal.

An attempt was made to fit the experimental data resulting from Eq. (V-4) to the integrated form of Eq. (V-5) where n is the fractional defect concentration.

$$\frac{dn}{dt} = -K_0 n^\gamma e^{-E_m/kT}. \quad (V-5)$$

γ was assumed to be either exactly equal to 1 or not equal to 1, since the integrated form of Eq. (V-5) will be logarithmic for the special case $\gamma = 1$. An attempt was made to obtain a fitted value of the parameters γ , K_0 , and E_m for the case $\gamma \neq 1$ and of K_0 and E_m for $\gamma = 1$. The input data was variously selected with the intent of representing only one physical process. As will be discussed further in Section VI, the results were generally not too satisfactory in that the quality of the fit, based upon the standard deviation, was poor. This was adjudged to be due to the small number of data points, and finally to the fact that there was apparently no unique or single process characterizing any of the sections of the isochronal curve. In view of the above complications the failure to obtain a good fit is not surprising; however, it is believed that this technique holds promise for other data where the above complications do not arise.

Data for the graphs of the numerical derivatives of the time corrected isochronal data were calculated from Eqs. (V-6) and (V-7) where x and y refer to the x and y axes which are temperatures and percent recovery, respectively. The i and $i-1$ indices refer to the i th and $i-1$ th data points.

$$\left(\frac{\Delta \text{Recov}}{\Delta T}\right)_i = \frac{y_i - y_{i-1}}{x_i - x_{i-1}} \quad (\text{V-6})$$

$$T_i = \frac{x_i + x_{i-1}}{2} \quad (\text{V-7})$$

The kinetics of a single recovery process can be determined by plotting $\ln (dn/dt)$ vs $\ln n$. As can be seen from Eqs. (V-5) and (V-8), the slope of this graph is γ —the reaction order.

$$\ln\left(\frac{-dn}{dt}\right) = \ln K_0 - E/kT + \gamma \ln n = \text{constant} + \gamma \ln n. \quad (\text{V-8})$$

In this form the data must all be taken at the same temperature. It is also possible to approximate an isochronal recovery curve constant where $T = \alpha t$, α being a constant. In this case dn/dT replaces dn/dt and the constant K_0 becomes K_0/α . If more than one process is active at a single temperature, we must generalize Eq. (V-8) as follows:

let $n = n_1 + n_2 + \dots$ where n_1 , n_2 , etc., are the concentrations of the different types of defects. Then Eq. (V-8) becomes

$$\frac{dn}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} + \dots = K_0^{(1)} n_1^{\gamma_1} e^{-E_1/kT} + K_0^{(2)} n_2^{\gamma_2} e^{-E_2/kT} + \dots \quad (\text{V-9})$$

In general a graphical solution is impossible; however, if all γ 's, K_0 's, and E 's are such that a function of $(n_1 + n_2 + \dots)^\gamma$ can be obtained then a graphical solution will still yield a straight line with a slope of γ . Otherwise the "straight" line will be curved. If any of the energies are dependent upon defect concentration (for example, $E = E_0 - \beta n$ where β is some constant), a graphical solution for γ will also yield a curved line. In practice, the former condition on the γ 's and K_0 's will almost guarantee the failure of a graphical solution.

If Eq. (V-5) is to be integrated it can be written as

$$\int_{n_1}^{n_2} \frac{dn}{n^\gamma} = \left(\int_{t_1}^{t_2} dt \right) K_0 e^{-E/kT} \quad (V-10)$$

The lefthand side of Eq. (V-10) is a pure number; in fact, even if the functional dependence of dn/dt is not n^γ but is some other $f(n)$, the integral between the two values of n is a constant. Thus, so long as the recovery occurs between the same limits, the expression

$$t e^{-E/kT} = \text{constant} \quad (V-11)$$

is valid, where t is the time required to go between the two limits. Utilizing Eq. (V-11) it is possible to superimpose the isochronal and isothermal recovery curves by noting that for recovery between the same two limits of n , Eq. (V-11) may be written

$$t_a e^{-E/kT_a} = t_i e^{-E/kT_i} \quad (V-12)$$

where the subscript i denotes the isothermal annealing process and a refers to the isochronal process. Rewriting Eq. (V-12) we find

$$\ln(t_i/t_a) = E/k \left(\frac{1}{T_i} - \frac{1}{T_a} \right). \quad (V-13)$$

For the isothermal process T_i is a constant, and for the isochronal process t_a is a constant. Hence we may write

$$\ln t_i = \text{constant} - E/kT_a. \quad (V-14)$$

From Eq. (V-14) it is obvious that a graph of $\ln t_i$ vs $1/T_a$ should be a straight line with a slope of $-E/k$. For $T = 11,607.9^\circ\text{K}$, $kT = 1$ eV. Thus if we plot $1,160.79/T_a$ the slope of the line will be in tenths of an electron volt, a convenient number for the low temperature (below 100°K) regime where activation energies generally range from 0.3 to 4.0 tenths of an electron volt.

Implicit in the above discussion is again the assumption that a single recovery process is responsible for all the change in n where it is to be remembered that the measured quantity is actually the total resistivity of the samples, and there is no way to distinguish directly

between resistivity changes due to different types of defects. With reference to Eq. (V-9) it can be seen that unless the functional dependence of dn/dt is such dn/dt can be written as a function of $n_1 + n_2 + \dots$ rather than simply as a function of $n_1, n_2, \dots$, integration such as in Eq. (V-10) is not possible. If, however, the proper functional dependence exists, Eq. (V-11) becomes

$$t \left(e^{-E_1/kT} + e^{-E_2/kT} \right) \dots = \text{constant}, \quad (\text{V-15})$$

and in principle a graphical technique such as described above would permit the determination of E_1, E_2 , etc. The necessary assumptions here are that $n_1 = n_2$ and that $\gamma = 1$. In practice, if there are more than two or three processes or if E_1, E_2 , etc., are not well separated, a graphical solution is not feasible. Under optimum conditions, however, the graph will show two or three distinct straight line segments, and by subtracting one line segment from another (curve stripping) it is possible to separate the two processes and determine E_1, E_2 , etc. One further assumption in the above is that the energy is not a function of the defect concentration. It might also be noted that if the energies are sufficiently different, the graph will still show two straight portions since, for example, all the n_1 might anneal out before any appreciable annealing of n_2 occurs if E_1 is much less than E_2 .

The graphical technique for determining the reaction order has one rather severe drawback: because the graph requires that the data be expressed in terms of the actual amount of the defect that is recovering in some given process it becomes necessary to convert from data where n refers to the concentration of all types of damage to data where n refers only to one specific type of damage. This requires a determination of the exact boundaries of the beginning and end of a recovery process. This must be determined from an examination of the isochronal recovery curve and its derivative. An estimation of the end of a recovery stage can also be made by extrapolating an isothermal recovery curve for that stage to long times; however, the starting point for the stage must be determined from the isochronal curve. When various recovery processes are not well separated in temperature a determination of the stage boundaries may contain considerable

error. Once the boundaries have been fixed, the total recovery, at some point in the stage, n , is renormalized by Eq. (V-16):

$$\text{Fraction of stage remaining} = \frac{n - n_e}{n_s - n_e}, \quad (\text{V-16})$$

where:

n_s = total recovery at the start of the stage

n_e = total recovery at the end of the stage.

The n used in Eq. (V-8) is the fraction of the stage which remains—that is, that given by Eq. (V-16). Because of the sensitivity of the renormalization procedure to the values of n_s and n_e , there may be a considerable error in the value of γ as determined from Eq. (V-8).

The above renormalization procedure is not necessary for the determination of the energy because the actual value of the integral between the two values of n need not be calculated since it is sufficient to know that it is constant and one need merely compare isothermal and isochronal recovery curves between the same two limits of total recovery.

One last point to note is that while physically the n in Eq. (V-5) refers to an actual number of defects, renormalization imposed by expressing n as some fraction of the total merely introduces another constant (the natural logarithm of the scaling factor) which may be incorporated in the constant K_0 so that the slopes corresponding to γ and E are not affected by the normalization process.

VI. DISCUSSION OF EXPERIMENTAL RESULTS

A. Review of Specific Recovery Modes and Models

In the course of the past 10 or 12 yr a considerable amount of work has been done on copper, silver, gold, and platinum, all of which have an fcc structure like thorium. Of these metals more work has been done on copper than on any other. There are many features of the recovery of radiation damage which is common to all of these metals and some features which are not. The particulars of the following discussion will pertain specifically to copper; however, the general features except where noted pertain to fcc metals in general.

Traditionally the recovery of radiation damage has been separated into five major stages, some of which have substages. The division is made according to temperature with the exact boundaries being somewhat arbitrary. For copper these stages are

Stage I	0°K to 60°K
Stage II	60°K to 220°K
Stage III	220°K to 330°K
Stage IV	330°K to 450°K
Stage V	T > 450°K.

For other fcc metals the boundaries are different and with the exception of gold tend to scale roughly as the melting point.

As has been noted in Section I, the details of the damage vary widely, depending upon the manner in which it has been introduced, with the damage becoming more complex as the mass and energy of the bombarding particle increases. The percentage recovery occurring in Stage I decreases as the complexity of the damage increases. Recent studies⁵³ have shown for low energy electron damage a graph of the amount of recovery vs the total dose introduced is roughly bell shaped with a maximum recovery of 85% for an introduced $\Delta\rho = 3 \times 10^{-9} \Omega\text{-cm}$ and a recovery of 60% for $\Delta\rho = 1.5 \times 10^{-11}$ and $\Delta\rho = 8 \times 10^{-7} \Omega\text{-cm}$. The introduction of impurities reduces the amount of recovery somewhat further. Stage I was first studied in detail by Corbett, Smith, and Walker.⁵⁴ Figure 6 shows some of their results. The various peaks were assigned the indicated nomenclature by them and this nomenclature has gained general acceptance. Figure 6, which is the numerical derivative of the isochronal recovery curve, was obtained from the isochronal data essentially as described in Section V.

The generally accepted equation governing the recovery of a single type of defect is

$$\frac{dn}{dt} = -K_0 n^\gamma e^{-E_m/kT}, \quad (\text{VI-1})$$

where:

n = defect concentration

t = time

Fig. 6. Derivative of the Stage I isochronal recovery curve for copper, as determined by Corbett, Smith, and Walker (after Ref. 6).

K_0 = pre-exponential factor, independent of T , which includes the entropy term and the attempt frequency

γ = reaction order

E_m = activation energy for the process

T = temperature in $^{\circ}\text{K}$.

In an isochronal recovery study where the time at each temperature is constant, the annealing process can be thought of as a constant heating rate with $T = At$ where A is a constant. Under these circumstances, $dT = Adt$ and Eq. (VI-1) becomes

$$\frac{dn}{dT} = -\frac{K_0}{A} n^{\gamma} e^{-E_m/kT}, \quad (\text{VI-2})$$

and it is seen that the temperature dependence of the defect concentration is exponential.

Substages I_A , I_B , and I_C represent single recovery processes with constant activation energies and may be completely described by Eqs. (VI-1) and (VI-2), with $\gamma = 1$. Substage I_D was later shown to contain substructure^{55,56} and appears to be due to a superposition of several different processes. The position of the center temperature in Stage I_E was found to be concentration dependent, implying that the reaction order was greater than one.

With the exception of gold, the recovery spectrum of most other fcc metals is qualitatively similar to Fig. 6. In gold Stage I accounts for far less of the total recovery than in copper. In addition the peak structure in Stage I is less well defined and the "background" annealing under and between the peaks is much larger in gold than in copper. There is also a relatively large amount of disagreement between independent studies in gold.

Two principal models have been proposed to explain the recovery of radiation damage in copper. These are the one interstitial model of Corbett⁸ and the two interstitial models of Seeger⁵⁷ and Meechan, Sosin, and Brinkman.⁵⁸ Both models agree on the following points:

1. The early part of Stage I is due to the recovery of close Frenkel pairs. The kinetics of close pairs involves only

the concentration of these pairs rather than the concentration of each of the constituents; hence close pair recovery is consistent with the observed first order kinetics.

2. Some type of interstitial migrates in Stage I.
3. Single vacancies migrate freely in either Stage III or Stage IV.
4. Defect recovery in Stage V is due to recrystallization.

As might be guessed from the names of the two models, the principal disagreement between the two models involves the question of where free interstitial migration occurs.

In the one interstitial model the interstitial migrates in the upper substages of Stage I. Stage I_D is ascribed to the correlated recovery due to the increased likelihood of a migrating interstitial finding its "own" vacancy. Stage I_E then corresponds to the long range diffusion of an interstitial which ultimately recombines with any other vacancy. Stage II and the first part of Stage III are ascribed to detrapping effects, that is, interstitials which have been trapped at impurities or grain boundaries are released from these traps and migrate rapidly to some vacancy and annihilate. The activation energy for this process is characteristic of the detrapping rather than the interstitial migration process. Free vacancy motion occurs in Stage III while Stage IV is characteristic of the detrapping of vacancies. Bauer and Goeppinger⁵⁹ have explained their platinum data with this model with the exception that free vacancy migration occurs in Stage IV. Minor variations of this model exist, but the essential features described above remain.

In the two-interstitial model, Stage I interstitial migration is ascribed to a special type of interstitial known as a crowdion—an extra atom fitted in along the $\langle 110 \rangle$ axis in an fcc metal. Stage III then corresponds to normal interstitial motion and Stage IV to free vacancy migration. Minor modifications of this model also exist.

A third model which has a lesser following than either of the others is a model proposed by von Jan.⁶⁰ Here, Stages I and II correspond to the recovery of "primary" and "secondary" close pairs where a secondary pair is a pair in which the interstitial and vacancy were not produced in the same event. These secondary pairs are

employed to explain the enhanced Stage I_E recovery which results from doping samples with excess vacancies prior to irradiation and annealing.

The ingenuity of the proponents of the various theories is sufficiently great that to date no truly definitive experiments have been devised to select the "correct" model.

B. Defect Production

These investigations were not designed to study defect production mechanisms; however, study of the rate at which the resistivity increases with time can yield information about such things as the size of the stable volume around each defect. The results of these studies are reported in this section.

As in the previous measurements the irradiation temperature was 4.2°K. No annealing occurs below 9°K so that all damage created at 4.2°K was retained.

The production of damage as was discussed in Section IV-C and in Section V was measured by the increase in sample resistance as a function of time. Due to the nature of the source of radiation, viz., α decay of ²²⁸Th with a 1.9 yr half-life, the flux was essentially constant over the course of the 3 to 4 days required to accumulate the damage necessary for an annealing run. Two samples were doped to approximately 0.6 and 3.0 ppm with ²²⁸Th. In order to calculate the total expected number of defects we assume that every α -decay creates the same number of defects and that all the decay products are retained in the samples. As mentioned in Section I-C, Vineyard³² estimates that 45% of the defects produced by self-damage in ²³⁹Pu are due to the α particles and 55% are due to the recoiling nuclei, and we will assume that this ratio also applies to thorium.

The range of 6 MeV α particles in lead is 17 gm/cm² and is relatively insensitive to atomic number. If we assume that this value also holds for thorium, and if we divide by the density of thorium and convert to inches, we find that the average alpha particle range is approximately 0.6 mils. A simple assumption is that one-half of the alpha particles which originate within one range of the surface will escape. (Alpha decay is isotropic so on the average one-half will be directed

towards the surface and one-half toward the center.) Of the escaping number, the average damage production is perhaps one-half of what it would be were the alphas completely contained. Based upon this estimate one-quarter of the alphas originating within 0.6 mils of each foil surface do not produce defects. In view of the cross-sectional dimensions (0.056 in. by 0.0025 in.) of the foil, edge effects may be neglected. The fractional loss of alphas is then just equal to $2 \frac{0.0006}{4} / 0.0025 = 0.12$ or 12%. Inasmuch as the alphas account for only 45% of the damage, the effective total damage is reduced by approximately 5%. While the above calculation is admittedly very crude, our knowledge of the number of defects produced per decay is even more uncertain so that more detailed calculations do not appear warranted. We can estimate the range of a ^{224}Ra recoil in a ^{232}Th matrix by utilizing the results of van Lint and Wyatt.⁶¹ They found that the range of the recoiling atoms scales roughly as $E^{0.7}$ where E is the recoil energy. They found experimentally that the range of 7.4 keV recoils was $38 \pm 1\text{Å}$. From the requirement of momentum conservation we find that

$$E_{\text{recoil}} = \frac{m_{\alpha}}{m_{\text{recoil}}} E_{\alpha} \quad (\text{VI-3})$$

For typical alpha energies such as given in Fig. 1 and summarized in Table 1, E_{recoil} is approximately 100 keV. This then gives a range of 235 Å or about 0.9×10^{-6} in. It can be seen that loss of recoil atoms is indeed negligible in view of the sample thickness of 2.5×10^{-3} in.

The number of disintegrations per unit volume, N , can be determined simply from the decay constant for ^{228}Th for which $\lambda = 1.15 \times 10^{-8}$ per second. The density of thorium is $11.7 \text{ g/cm}^3 = 3.0 \times 10^{22} \text{ atom/cm}^3$; therefore, $N = 4.5 \times 10^{14} \text{ disintegrations/cm}^3/\text{sec}$. If we now multiply by the atomic fractions of ^{228}Th in ^{232}Th which were 0.6×10^{-6} for Sample 1, and 3.0×10^{-6} for Sample 2, and if we then multiply by 5 since each ^{228}Th decay results in a total of five alphas and five recoil nuclei, we find that there were $6.7 \times 10^9 \text{ disintegrations/cm}^3/\text{sec}$ in Sample 1 and $1.3 \times 10^9 \text{ disintegrations/cm}^3/\text{sec}$ in Sample 2. Remembering the estimate of 1800-2000 pairs per disintegration we see that there were roughly $10^{12} - 10^{13}$ Frenkel pairs produced per cm^3/sec .

If we assume that the defects are produced with a random distribution, then the rate at which Frenkel pairs are produced can be written as

$$\frac{dn}{dt} = \sigma_d \psi (1 - 2 V_S n), \quad (\text{VI-4})$$

where:

n = Frenkel pair concentration = number of Frenkel pairs per unit volume

σ_d = number of Frenkel pairs produced per alpha decay

ψ = number of alpha decays per unit volume per unit time

V_S = spontaneous recombination volume.

The spontaneous recombination volume is discussed in detail in Ref. 52. Basically it is the volume around a defect within which any newly created defect will spontaneously recombine with the defect at the center of the volume, provided of course that the two defects are of the opposite type. In Eq. (VI-4) the first term is the total number of defects produced per unit volume; the second term is the number per unit volume which spontaneously recombine. The factor of 2 is due to there being two defects in a pair.

Making use of the relations

$$\Delta \rho = n V_A \Delta \rho_F, \quad (\text{VI-5})$$

where V_A is the atomic volume and $\Delta \rho_F$ is the resistivity increment per atomic fraction of Frenkel pairs, and the fact that

$$\frac{\Delta \rho}{\rho_0} = \frac{\Delta R}{R_0}, \quad (\text{VI-6})$$

where ρ_0 and R_0 are the redual values of resistivity and resistance, respectively, we can write Eq. (VI-4) in terms of ΔR as

$$\frac{d\Delta R}{dt} = \frac{\sigma_d \psi R_0 V_A \Delta \rho_F}{\rho_0} - 2 \sigma_d \psi V_S \Delta R. \quad (\text{VI-7})$$

There are three unknown quantities in the above equation:

σ_d , V_S , and $\Delta \rho_F$.

Equation (V-2), which is rewritten here as Eq. (VI-8),

$$\frac{d\Delta R}{dt} = \phi - \alpha \Delta R, \quad (\text{VI-8})$$

gives the increase in resistance as a function of time.

We can estimate $\Delta\rho_F$ for thorium from the value of ϕ . The assumption required here is the value of σ_d , the number of defects produced per decay. We have estimated this to be 2000 defects per decay. Using the fitted value of $\phi = 4.397 \times 10^{-5} \mu\Omega/\text{min}$ for Sample 1, the decay rate (for 3 ppm ^{228}Th) of 6.7×10^9 disintegrations/ cm^3/sec , and the correspondence between ϕ in Eq. (VI-8) and the first term in Eq. (VI-7), the resistivity increment, $\Delta\rho_F$, is calculated to be about 3000 $\mu\Omega\text{-cm}/\text{atomic fraction}$; or 30 $\mu\Omega\text{-cm}/\text{at.}\%$; however, the error bars, in view of the approximations involved in the σ_d , must be from ± 25 to $\pm 50\%$.

Given a value for the defect resistivity it then becomes possible to estimate the recombination volume using the ratio of α/ϕ where α and ϕ are as defined in Eq. (V-2) which was rewritten here as Eq. (VI-8). Comparison of the form of Eq. (VI-8) with that of Eq. (VI-7) permits the analogy

$$2V_S = \frac{\alpha}{\phi} \frac{R_0}{\rho_0} \Delta\rho_F V_A. \quad (\text{VI-9})$$

From the computer fitted values of $\alpha = 2.338 \times 10^{-5}/\text{min}$ and $\phi = 4.397 \times 10^{-5} \mu\Omega/\text{min}$, and with $\rho_0 = 0.68 \mu\Omega\text{-cm}$, $\Delta\rho_F = 3000 \mu\Omega\text{-cm}/\text{atomic fraction}$ and $R_0 = 2.5 \times 10^{-3} \Omega$, a value of about 2900 atomic volumes is arrived at for V_S . The value is considerably larger than reported values⁵² for V_S of a few hundred atomic volumes for other fcc metals. It should be pointed out, however, that much of the other work involved low energy electron damage rather than heavy particles (recoil nuclei) as was the case in the present work. In view of the nature of heavy particle damage it would be anticipated that substantial radiation annealing might occur due to thermal spikes, and in view of the observed high value of V_S , this appears to be the case here. Thus, the observed rate of change of the defect production rate cannot be explained in terms of a simple recombination volume, but reflects the

additional annealing contribution due to the dynamical recombination processes characterizing heavy particle damage.

C. Stage I—Stage IV Recovery

The results of a 15 min isochronal anneal of Samples 1 and 2 are presented in Fig. 7. In Fig. 8 is presented the numerical difference in the percent recovery of Samples 1 and 2. Sample 1 was doped to approximately 3 ppm and Sample 2 to 0.6 ppm ^{228}Th , as previously mentioned. The total amount of damage introduced in the two samples differed by slightly less than a factor of 5 due to the effects of radiation annealing as discussed in the previous section. The samples were pre-irradiated at an average temperature of 79°K to the values of $\Delta\rho_D$ given in Table 3; they were then cooled to 4.2°K and damage, $\Delta\rho_0$, was accumulated as noted in Table 3. The basic sample resistivity at 4.2°K, $\rho_0 = 0.68 \mu\Omega\text{-cm}$, is uncertain to $\pm 10\%$ due to inaccuracies in the values of cross-sectional area and gauge length; however, relative values of the resistivity are accurate to a few parts in $10^{-5} \mu\Omega\text{-cm}$. Thus, the low temperature recovery was characteristic of radiation doped recovery. Stage I, and Stage II below 80°K, were studied in much greater detail than shown in Figs. 7 and 8, and these results are presented in Section VI-D. The percent recovery shown in Fig. 7 was scaled since the baseline for recovery below 79°K was different by about a factor of 5 from the baseline for recovery above 79°K. The scaling was such that the total recovery for temperatures above 79°K which was relative to the absolute baseline following the 1100°K preliminary annealing would represent at most that amount of damage which was still stable at 75°K (this temperature was arbitrarily selected) following the annealing of the damage accumulated at 4.2°K.

The cryostat was designed to optimize stable temperature control rather than rapid cycle time and the temperature steps were rather larger and therefore do not delineate the exact position of the stages. The approximate boundaries of the recovery stages in thorium are as follows:

Stage I	below 48°K
Stage II	48°K to 230°K

Fig. 7. 15-min isochronal recovery curve (4.2 to 1150°K).

Fig. 8. Difference in percent total recovery (90 to 1150°K), Sample 1-Sample 2.

Stage III	230°K to 400°K
Stage IV	400°K to 1100°K
Stage V	above 1100°K

Some recrystallization has been observed in thorium at temperatures as low as 800°K;^{38,39} however, sample purity plays an important role in the temperature dependence of the recrystallization process. In this particular batch of metal recrystallization was visually obvious after annealing at temperatures above 1250°K, but was not visible for temperatures below 1250°K. This batch of thorium metal undergoes a phase transformation from fcc to bcc at $1636 \pm 10^\circ\text{K}$ and melts at $1963 \pm 10^\circ\text{K}$. From the above it can be seen that the upper boundary of Stage IV is quite arbitrary and some recrystallization may indeed be occurring at temperatures above 800°K. As discussed in Section IV-D, the error bars in temperature for data points above 500°K are due to the necessity to determine the temperature based upon sample resistance and an extrapolation of dR/dT over several hundred degrees.

Table 3. Radiation Damage and Doping Levels

Data run	$\Delta\rho_D (\mu\Omega\text{-cm})$ 79°K radiation doping level		$\Delta\rho_0 (\mu\Omega\text{-cm})$ 4.2°K radiation damage level ^a	
	1	2	1	2
15 min isochrona..	0.2612	0.0560	0.0386	0.0095
10 min undoped isochronal No. 1	—	—	0.0756	0.0172
10 min undoped isochronal No. 2	—	—	0.0756	0.0172
10 min heavily doped isochronal	0.4803	0.1160	0.0700	0.0687
Undoped isothermals (19.1°, 31.1°, 57.7°K)	—	—	0.0590	0.0116
Lightly doped isothermals (17.0°, 31.1°, 57.5°K)	0.0566	0.0127	0.0742	0.0153
Heavily doped isothermal (37.8°K)	0.5012	0.1217	0.0700	0.0181

^aThe basic undamaged sample resistivity at 4.2°K,
 $4.2 \rho_0 = 0.68 \mu\Omega\text{-cm}$.

One of the principal higher temperature recovery features occurs in the temperature range from about 275°K to 375°K. This is tentatively assigned to vacancy migration which thus would be assigned to Stage III rather than Stage IV. The two-interstitial model, however, would permit this recovery to be due to the second interstitial and this possibility cannot be precluded. It must be admitted, however, that on the basis of the small amount of data gathered here, the above assignment is somewhat arbitrary.

The other principal feature of the damage recovery is best shown in Fig. 8 and is the dependence of the recovery upon the total amount of damage present. A graph such as Fig. 8 tends to overemphasize the importance of minor differences, inasmuch as the scatter in the difference is approximately 1.6. Hence, while fine structure is of little significance, major trends are clear. The only temperature range where the less damaged sample shows greater recovery than the more heavily damaged sample is from about 90-200°K and the total differential is nearly within the limits of experimental error. At temperatures above about 250°K the more heavily damaged sample exhibits the greater recovery by a clear margin. To understand this, it is important to remember that we are actually dealing with a relatively small fraction of the saturation value for the damage. In fact, the relative concentration of specific types of defects introduced in both samples is less than the impurity concentration. Even in the more heavily damaged sample the total number of defects introduced was only approximately equal to the impurity concentration; hence, the number of any primary type of defect such as vacancies or interstitials might be expected to be at best roughly equal to the impurity concentration. With this in mind it is possible to explain some of the features of Fig. 8 in terms of impurity effects. Any recovery mechanism involving intermediate or long range diffusion of a defect will be influenced by impurity trapping. It will be observed that a recovery differential was established in the temperature range from 250-350°K and was maintained at a more or less constant value up to about 800°K, above which temperature the differential gradually disappeared. The 250-350°K temperature range is a major portion of what we have defined as Stage III, and the steepest part of the peak occurs from

275-350°K—the temperature at which free vacancy (single interstitial model) or free interstitial (two interstitial model) migration most probably occurs. Thus, it appears that the same absolute number of vacancies or interstitials are trapped in both samples, but that percentage-wise this is a much larger effect in the less damaged number two sample so that its recovery is rather more inhibited than that of the more heavily damaged No. 1 sample. At higher temperatures where detrapping of the mobile defect occurs the recovery in No. 2 finally catches up with that of No. 1. The above model of course grossly oversimplifies the high temperature recovery process since vacancy and interstitial clusters will also be breaking up and migrating; however, the principal feature is the apparent threshold level of damage above which the impurity dominated "trapping background" becomes insignificant. The only possible preference (aside from prejudice) for vacancies over interstitials is that the principal impurity in thorium was found to be carbon (see Section III-A) which is an interstitial impurity which would thus be more likely to trap vacancies than interstitials; however, interstitial trapping by interstitial impurities is also fairly common.

D. Isochronal and Isothermal Recovery in Stage I

The results of two identical 10-min isochronal anneals for Samples 1 and 2 are presented in Figs. 9 and 10 respectively. The damage levels are listed in Table 3. Figure 11 is a presentation of the numerical derivative of the curves in Figs. 9 and 10. In Fig. 12 the difference in the amount of recovery of Samples 1 and 2 is presented as a function of temperature, and in Fig. 13 the difference in the doped and undoped recovery of Samples 1 and 2 is presented. In addition, the data points shown in Figs. 9 and 10 for the heavily doped 10-min isochronal are plotted to permit comparison.

The data shown in Figs 9 and 10 for the two undoped isochronals were obtained under virtually identical conditions; the samples were given a high temperature anneal, as described in Section IV-C, and were then stored at 4.2°K for 4-1/2 days allowing the damage to accumulate. The first isochronal required about 15 hr to perform, while the second required about 16-1/2 hr to perform. As can be seen in

Fig. 9. 10-min isochronal recovery curve—Sample 1, Stage I.

Fig. 10. 10-min isochronal recovery curve—Sample 2, Stage I.

Fig. 11. Numerical derivative of isochronal recovery curves.

Fig. 12. Difference in percent total recovery (4.2 to 80°K).

Fig. 13. Effect of radiation doping on percent total recovery—
Samples 1 and 2.

Figs. 9 and 10, the reproducibility of the data is excellent. It will be noted that the only real disagreement involves the data points at 69.7° and 73.0° taken during the first isochronal run. The probable reason for this is that during the first isochronal run the temperature range from 57.1 - 69.8° was accidentally missed and in the anger of the moment, less care was taken in acquiring the next couple of data points. The scatter in the data for Sample 2 is somewhat greater than that for Sample 1 due to the smaller amount of damage introduced in the second sample.

One of the first things one notices about Stage I recovery as depicted in Figs. 9 and 10 is that the total recovery is somewhat less than 40% (actually only about 30% at 48° which is the upper limit of Stage I). This is in marked contrast with previously discussed electron damage results where typically 75-85% recovery is observed in Stage I. Very recent 2 MeV electron irradiation of thorium has been performed by Snead, Guinan, and Goland at Brookhaven National Laboratory, utilizing a sample made by us from a piece of thorium metal which was cut from the undoped standard sample employed here. The only additional handling was another rolling operation which thinned the sample to a thickness of slightly less than 0.002 in. While the electron damage data have not yet been fully analyzed, recovery of more than 70% of total damage was observed in Stage I. The amount of damage introduced by electrons was roughly equal to one-third of the amount introduced in our low damage sample and was also less than the amount of electron damage required to produce "maximum" recovery as determined from the bell shaped recovery-vs-dose curve in Ref. 53. The resistivity ratio of the electron irradiated sample was only 11:1 as compared to our doped sample which was 19:1; however, the former was severely cold worked (almost to the point of cracking) and the annealing treatment which was below 1000°C may not have removed it all. In any event, the difference in the amount of Stage I recovery is striking. In work by Bauer, Herschbach, and Jackson⁶² Stage I recovery of electron damage in titanium is about 80% while alpha damage recovery is about 60%. In deuteron produced damage in platinum, Jackson and Herschbach⁶³ found approximately 60% recovery in Stage I.

The drastic reduction in Stage I recovery in thorium can be explained in terms of the type of damage created and the effect of

impurities. In view of the damage due to recoil nuclei as well as the relatively massive nature of alpha particles, one might well expect that fewer close pairs would be created, that interstitial and vacancy clusters, many containing appreciably more than two defects, would be produced, and that considerable delocalization of the damage would result due to focusing, channeling, and simply to the high energy transfers involved. As a result close pair recovery and some short range correlated recovery should be suppressed in these samples.

In the electron damaged thorium the percentage recovery in Stage I_D was comparable with that observed in the present alpha study, but Stages I_A, I_B, and I_C represented about 40% of the total recovery for electron damage and only 8% for alpha damage. This discrepancy is believed to be due to the relative lack of close pairs in the alpha damaged samples.

The preliminary data from electron damage indicate a nearly one to one correspondence to the peaks shown in Fig. 11, with the electron produced peaks appearing to be shifted to somewhat lower temperatures. As mentioned, however, the relative heights of the peaks differ significantly. The smooth curves drawn in Fig. 11 are somewhat arbitrary in places, but the low temperature peak around 11° appears to be real, and there definitely appears to be some sort of peak centered in the vicinity of 41°. There is some definite structure in the peak(s) located around 20° but the exact form of the structure is not well determined. The exact shape and center of the peak(s) located around 57-58° are also in doubt, but the general features are well defined.

The differences in the recovery of the two alpha and recoil damaged samples can be seen in Figs. 12 and 13. The solid line drawn in Fig. 12 is a somewhat arbitrary average of the data from the two isochronals, but again the general features are correct. Here too it should be remembered that the scatter in the data in Fig. 12 is about 0.6 of 1%. The principal feature of interest is the peak located at 35°.

A point to notice in Figs. 9 and 10 is that the heavily predoped isochronal generally follows the undoped isochronal up to the 30-40° range. Between 30° and 40° the annealing in the predoped samples as compared to the undoped samples is substantially enhanced, with the

enhancement being especially pronounced in the case of the heavily damaged sample. Figure 13 displays the enhanced recovery quite clearly as a difference in the amount of recovery between the doped and undoped samples. As was the case in Fig. 12, the heavily damaged sample displays the greater amount of recovery in the 30-40° temperature range.

The data in Fig. 11 can be qualitatively understood as being virtually identical to the assignments made to recovery peaks in copper, with there being five substages in Stage I, with Stage II beginning at about 48°K. Substages I_A , I_B , and I_C are due to the recovery of various types of close pairs or the reorientation of different clusters. There really is no firm evidence for this assignment other than the general agreement of this assignment in other fcc metals. As will be seen later, an activation energy determined in two different ways is approximately the energy one would expect for this type of recovery. Stage I_D is assigned to correlated recovery of some type of defect, probably the annihilation of a migrating interstitial with its "own" vacancy. Finally, Stage I_E is thought to be free interstitial migration. These latter two assignments will be discussed below.

Remembering that Sample 1 will always contain from four to five times as much damage as Sample 2, the principal features of the data as presented in Figs. 8-13 which pertain to Substages I_D and I_E are the following:

1. Sample 1 recovers much faster than Sample 2 in the vicinity of 30-40°K. This is true of both predoped and undoped runs.
2. Both predoped samples exhibit greatly enhanced recovery relative to the undoped samples between 35° and 40°.
3. Figure 11 shows the existence of a small "shoulder" on the right side of the principal peak.
4. The heavily radiation doped samples display substantially enhanced recovery in the 30-40° temperature range.
5. In the radiation doped samples, the enhanced recovery between 30° and 40° is more pronounced in Sample 1 than in Sample 2.

6. The enhanced recovery of Sample 1 begins at a lower temperature than that of Sample 2.
7. In Fig. 11, the I_D peak appears to have been broadened asymmetrically on the right side in the case of the radiation doped run.

This data can be explained in the context of both the one and two interstitial models formulated to explain radiation damage recovery in copper. The greatly enhanced recovery obtained by radiation doping, which introduces excess vacancies, can only be explained by free migration of some interstitial. The probability of interstitial-vacancy annihilation as opposed to the trapping of the interstitial is greatly enhanced by the excess of vacancies. With this in mind the seven points listed above are explained as follows:

1. The I_D peak involves correlated recovery of an interstitial and "its" vacancy and is characterized by short range interstitial migration.
2. The "shoulder" seen in Fig. 11 is Stage I_E and is nearly hidden by the larger I_D .
3. Long range interstitial migration occurs in Stage I_E .
4. In the heavily radiation doped samples, Sample 2 which has roughly one-fifth as much damage per unit volume as Sample 1, will thus have a mean interstitial-vacancy distance which is $3\sqrt{5} \approx 1.7$ times as great as that of Sample 1. Hence, a migrating interstitial in Sample 1 need make a lesser number of jumps to find a vacancy, and thus enhanced annealing due to long-range interstitial migration will begin to occur at somewhat lower temperatures in Sample 1 than in Sample 2.
5. The apparent asymmetric broadening of the I_D peak in the radiation doped runs of Fig. 11 is caused by the enhancement of the I_E peak and its shifting to a slightly lower temperature as a result of the reduction in the mean interstitial-vacancy separation.

In an attempt to determine the reaction order and characteristic energy, and to demonstrate free interstitial migration, isothermal irradiations were performed at 1) 17° and 19.1°; 2) 31.1° and 31.1°; and

3) 57.5° and 57.7°. In the first of each of these isothermals the samples had been lightly predoped by not annealing out the damage remaining at the conclusion of the second 10 min undoped isochronal. Following the acquisition of the last data point in the isochronal the samples were stored at 4.2°K for 4-1/2 days and then isothermal anneals were performed at 17°, 31.1° and 57.5 ± 0.1°. The doping and damage levels are given in Table 3. At this time the 57° peak was believed to be the long range diffusion process. Following this series of isothermals the samples were annealed at 1150°K and then stored again for 4-1/2 days at which time the second set of isothermals was taken. The 19.1° temperature was selected to increase the amount of recovery and decrease the time required to perform the annealing. Radiation doping was not expected to greatly affect the close pair type of recovery. It was intended to perform the other two annealing operations at the same temperature as before in order to demonstrate the effect of radiation doping. The doping ratio was approximately 0.8:1, that is, there was initially 0.8 times as much damage remaining from the previous isochronal as there was total damage introduced in storage at 4.2° prior to the start of the second isothermal series. Figures 14 and 15 present the relevant data from these isothermals, as well as data from a heavily radiation doped isothermal anneal which will be discussed later. In Fig. 14 the anneals for the doped vs undoped samples is presented. In the case of the 17° and 19.1° anneals, no real comparison is possible due to the temperature difference. The $t = 0$ point for the 13.1° isothermals was established by annealing for 10 min at 25°. At 13.1° there is a very slight tendency for the undoped sample to anneal faster than the doped sample, but the difference is only slightly greater than the experimental scatter in the data. In any event this tendency can be explained in terms of the more gross nature of the residual damage in the doped case. With a greater amount of gross damage there would be some reduction in the amount of correlated recovery. The 31.1° isothermal only followed recovery up to a point equivalent to the recovery obtained by a 10 min anneal at 35°K and thus was not representative of any process occurring above 35°K.

The two isothermal annealing curves obtained at 57.5° and 57.7° are rather interesting. They are identical with the exception of a

Fig. 14. Isothermal recovery curves—Sample 1.

Fig. 15. Isothermal recovery curves—Samples 1 and 2 at identical temperatures.

3.6% offset. The predoped annealing curve has been plotted twice in Fig. 14. The original curve is that curve denoted by the triangles. The same curve, shifted upward by 3.6% is denoted by the square symbols. As can be seen the replotted curve is coincident with the undoped curve. This is indicative of the fact that the process which occurs at about 57° is completely unaffected by the radiation doping process. What has happened is that there has been a big change in the recovery process between 31° and 50°. The $\theta = 0$ point for the 57.5° and 57.7° isothermals was the recovery obtained after a 10 min anneal at 50°. The observed result is, of course, consistent with what was observed in Figs. 9, 10, and 13, that is, enhanced recovery between 35° and 40° due to long range interstitial migration.

In Fig. 15 a comparison of the recovery curves for Samples 1 and 2 is presented. With the exception of constant offsets stemming from the low temperature recovery history, the recovery curves are identical within experimental error. No comparison of the lowest temperature (17° and 19.1°) curves was possible due to the large scatter in the data for Sample 2. This large scatter was due to the fact that the total amount of recovery involved was small, and the absolute amount of recovery was only about 12 parts in 10^5 for this sample whereas the experimental scatter was ± 2 parts in 10^5 , and the first couple of data points account for about 80% of the total recovery. The recovery curves in Fig. 15 are typical of the same comparison for the undoped samples, so these data are not presented.

The information obtained from examination of these isothermal recovery curves alone can be summarized by saying that the processes occurring at 31.1° and 57.5° are essentially unaffected by the radiation doping process; however, the doping levels were rather low. In view of the two different temperatures at which the two low temperature isothermals (17° and 19.1°) were obtained, no direct assessment of the effect of predoping can be made. The only important question which arose from the two series of isochronals was the question about the 3.6% recovery enhancement which had occurred somewhere between about 35° and 50°K.

As a consequence of the results of the two isothermal series, a heavily doped isochronal run was performed, the results of which were

presented in Figs. 9, 10, 11, and 13. Following this, yet another isothermal run was made at 37.8°K in order to cover the 35-40° recovery region. The radiation doping and damage levels for these runs are also given in Table 3, and the results are discussed later. As has been mentioned, this 37.8° isothermal recovery curve is also presented in Fig. 14.

An attempt was made to determine the reaction orders, γ , for the various processes in the manner discussed in Section V. In the case of the low temperature data there was a pronounced curvature to the plot of $\ln (\Delta n / \Delta t)$ vs $\ln n$ indicating that there is no unique process active in that temperature range, but rather that two or more processes are active. This is in agreement with Fig. 11 where Stages I_B and I_C are not clearly separated. The slope of a line drawn through this data is not really significant in view of the multiple processes. There was no definite curvature in the corresponding graph of the data for 31.1° but due to the scatter, straight lines with a slope ranging from 2-3 can be drawn. The "best" line has a slope of 2.6. Many observers have found reaction orders greater than two in correlated recovery, and Fujita and Damask⁶⁴ have analyzed bimolecular reactions involving unequal concentrations of reactants and have found that while the expected reaction order of two is obtained for $D_i/C_i = 1$ (C_i and D_i are defined as the initial concentrations of the reacting species C and D), the apparent reaction order is about 1.2 for $D_i/C_i = 2$, while the apparent order is 4 for $D_i/C_i = 0.5$ and 10 for $D_i/C_i = 0.2$. As discussed in Section V, the slope of the $\ln (\Delta n / \Delta t)$ vs $\ln n$ curve depends upon the normalization process. The end of the stage was assumed to correspond to the amount of total recovery represented by extrapolation of the isothermal recovery curves in Fig. 14 to long times. If instead, the recovery corresponding to 48-50° were employed as a criterion for the cutoff point, a reaction order near 5 would be obtained for the 31.1° process. The significant fact here is that the observed reaction order is not inconsistent with the assumption of the correlated recovery of some defect, and it is certainly plausible, in view of the nature of the damage process, that the concentrations of the various reactants might not be equal. A similar analysis of the 37.8° isothermal produced results similar to those of the 31.1° isothermal.

By superimposing the isochronal and isothermal recovery curves as discussed in Section V, it is possible to determine the activation energy for the process, assuming that there is a unique process operating, or that if two different processes are active, they must both have the same functional dependence upon the concentration of the species involved, or finally, under other assumptions, if all processes have the same activation energy. These conditions are discussed in detail in Section V, as in the superposition technique.

The results of superimposing the isochronal and isothermal recovery curves is shown in Figs. 16-19. In Fig. 16 it is seen that a straight line can be fitted to the data and the energy thus obtained is 0.0207 ± 0.004 eV, a number which is lower than the $0.027\text{--}0.050$ eV⁸ found for the low temperature stages in other fcc metals. For this lowest temperature stage isothermal anneals were performed at two different temperatures, permitting the use of an independent technique (crosscut method--see Section V). The application of this technique to the 17° and 19.1° isothermals yields a value of 0.021 ± 0.002 eV, in agreement with Fig. 17. The limits of error for the crosscut technique are different due to the fact that a slightly different energy is found depending on the value of n at which the crosscut is taken. This is indicative of the presence of more than one process, as has been surmised from the other data. While the "common" activation energy appears somewhat low, it is to be noted that if the reaction order were greater than 1 for one or more of these processes as would appear possible from the attempts to determine γ , then a low value for the energy would be expected. The existence of a reaction order greater than 1 for close pair recovery would require that the process be a bimolecular reaction in which the close pair recovery was actually a form of correlated recovery in which a given reactant was sufficiently close to form a "close-pair" with more than one of the other species, thus resulting in a bimolecular reaction with $D_i/C_i \neq 1$. In view of the gross nature of the damage this cannot be ruled out. Further work would be necessary to fully establish the nature of Stages I_A, I_B, and I_C.

Figure 17 yields a well defined activation energy of 0.0875 eV for the 31.1° process. This is in general agreement with energies found for Stage I_D.⁸ The 31.1° isothermal recovery curves shown in Fig. 14

Fig. 16. Energy determination for Stage I_B.

Fig. 17. Energy determination for Stage I_D .

Fig. 18. Energy determination for Stage I_E.

Fig. 19. Energy determination for Stages Π_A and Π_B .

did not include the recovery beyond that which would represent Stage I_E . The 37.8° isothermal recovery curve, however, did monitor the Stage I_E recovery region and was utilized in conjunction with the heavily doped isochronal recovery curve to determine an activation energy for this stage. The energy was determined to be 0.0869 eV which is in agreement with the energy found for I_D (Fig. 18), within the limits of the probable errors of ± 0.002 eV and maximum possible errors of about 5%. The evidence for long range interstitial migration in Stage I_E now appears to be quite conclusive: greatly enhanced recovery was obtained by radiation doping which introduced an excess of vacancies, and Stages I_D and I_E were found to have essentially the same activation energy. The requirement of identical activation energies is imposed by the nature of correlated recovery and long range interstitial migration. Correlated recovery is free interstitial migration over a short distance whereupon the interstitial finds its "own" vacancy. Long range migration is free interstitial migration over a relatively large distance, culminating in the annihilation of the interstitial at some vacancy other than its "own." Both processes, however, involve free interstitial migration and thus should have identical activation energies.

In Fig. 19 it is found that there are two straight line portions of the graph. As discussed in Section V, this is indicative of the existence of more than one process as might be anticipated from the skewed nature of the 55° peak in Fig. 6. If one makes the assumption that the faster of the two processes occurs so fast that all of its recovery is complete prior to any appreciable recovery of the slower process, then each of the two straight line sections of Fig. 19 represents the activation energy for its process. This assumption is not necessarily valid here, and the magnitude of the error in the assumption cannot be determined. The conventional "curve stripping" techniques of activation analysis are not applicable to plots such as Fig. 19, unless, as discussed in Section V, the reaction order for both processes is equal to 1. As previously discussed the reaction order for these processes is approximately 2.6. Nevertheless, the slopes of the two straight line portions of Fig. 19 give energies of 0.100 eV and 0.278 eV. The error limits on these values are approximately ± 0.01 eV due to the reduced portion of the original data which is available for determining the slopes

of the lines. In view of the duality of this recovery process the two processes have been labeled Π_A and Π_B in accordance with the accepted nomenclature for Stage I. As was noted earlier the upper boundary of Stage I has been set at 48° in view of the form of peak structure found below that temperature.

VII. SUMMARY AND CONCLUSIONS

We have investigated the feasibility of producing radiation damage in metals by homogeneously doping thorium in the melt with a short-lived isotope (^{228}Th) whose decay produces the radiation damage which can then be studied by conventional techniques such as electrical resistivity, internal friction, etc. It was found possible to prepare the samples without introducing more than a few parts per million of impurities. The principal advantages of such a technique are as follows:

1. No accelerator or reactor is necessary.
2. The irradiation procedure is greatly simplified.
3. The sample holder and cryostat design are simplified.
4. The cost of the experiment is reduced.
5. Heavy particle damage can be produced and studied easily.
6. The entire sample is homogeneously irradiated.
7. There is no problem in maintaining the sample temperature as low as is desired.

The principal disadvantages are as follows:

1. With the exception of high energy beta emitters, the recoil nuclei will introduce heavy particle damage which, by its gross nature, may make the data more difficult to interpret.
2. Sample preparation becomes more difficult, primarily due to potential handling difficulties associated with the dopant material prior to mixing.
3. With this type of experiment threshold studies and other studies requiring the variation of the "beam" energy become impractical.

For many types of radiation damage studies it is felt that the advantage of techniques similar to those described here far outweigh the disadvantages.

A rough isochronal anneal covering the temperature range from 4.2-1150°K has been performed. This isochronal covers Stage I through Stage IV, and the boundaries of the various stages are approximately

Stage I	4.2° to 48°K
Stage II	48° to 230°K
Stage III	230° to 400°K
Stage IV	400° to 1100°K
Stage V	above 1100°K.

Vacancy migration is tentatively assigned to Stage III, but the evidence is weak and further work is required to establish the nature of Stage III.

Stage I has been studied in greater detail than the others with 2.5° step isochronals and with isothermals at temperatures in the middle of major recovery peaks. Five recovery peaks are found in Stage I in analogy with copper; however, these peaks are not as well defined as in copper. The sources of the various substages are believed to be the same as in copper, and Stage I_E corresponds to the long range migration of an interstitial.

The total Stage I recovery in annealed thorium was only about 30% of the total damage. It is supposed that this low value was due to the gross nature of the damage created by the 5-7 MeV alpha particles and the 100 keV recoil nuclei. It was found in recent work using 2 MeV electrons (see Section VI-D) that more than 75% recovery occurs in Stage I. The peak structure found here was qualitatively the same as found in the electron damage work.

Activation energies were found for Stages I_B , I_D , I_E , and II_A and II_B . Stages I_B and I_C were found to have a common activation energy of about 0.021 ± 0.002 eV. Stage I_D had an activation energy of 0.0875 ± 0.002 eV and Stage I_E was found to have an activation energy of 0.0869 ± 0.002 eV. In addition, the introduction of a large excess vacancy concentration by long term irradiation at a temperature above Stage I considerably enhanced the rate of recovery in the temperature range corresponding to Stage I_E . Hence, it is concluded that Stage I_D represents correlated interstitial recovery, and Stage I_E represents long range interstitial migration. Stage I_D , by far the most prominent substage, was found to have an apparent reaction order greater than 2.

This was explained in terms of a bimolecular reaction involving unequal reactant concentrations.

Stages II_A and I_B were found to have a common reaction order of 2.6. However, the activation energies for the two processes were not the same. Under the somewhat restrictive assumptions discussed in Sections V and VI-D, activation energies of 0.100 ± 0.01 eV and 0.182 ± 0.01 eV were obtained for these processes.

The damage rate was not a linear function of the dose and the initial damage rate and the curvature in the damage rate were analyzed to obtain approximate values for the resistivity increment per atomic percent Frenkel pairs ($30 \pm 15 \times 10^{-6} \Omega\text{-cm}$) and for the spontaneous recombination volume (2900 atomic volumes). The excessive value of the latter was interpreted to indicate the existence of appreciable recombination due to thermal spikes.

Two samples, differing in doping level by a factor of 5, were studied and some minor differences in the data were found and discussed. Considerably more work remains to be done in this area.

Thorium appears to be very similar to copper and further detailed and controlled electron damage work, particularly in Stage I and Stage III, should prove quite fruitful.

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