

THE DISPLACEMENT OF ATOMS IN SOLIDS BY RADIATION

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SYNOPSIS

Two questions are raised by phenomena observed in irradiated solids. What kind of defects are produced? How do such defects alter the properties of the solids? For both questions the answers, in so far as they are known, vary widely from one type of solid to another and, rather less markedly, from one type of radiation to another. In molecular compounds and plastics, the changes observed are largely a consequence of chemical rearrangement induced by ionization. In ionic compounds also, the majority of the effects studied arise from ionization, although the processes involved have been thought of in physical rather than in chemical terms. In metals and covalent compounds, large changes are induced by the displacement of atoms from their lattice sites by collision processes, and the defects produced are primarily interstitial-vacancy pairs, that is, Frenkel defects. This article is mainly concerned with this last case.

Theoretical and experimental work shows that about 25 ev has to be transferred to an atom to form a Frenkel defect. When an atom is displaced by direct collision with the bombarding radiation, we refer to it as a primary knock-on. In some cases, notably electron irradiation, the majority of the displaced atoms are primary knock-ons. In other cases, notably fast neutron irradiation, the majority of the displaced atoms are produced as a consequence of the collisions made by the primary knock-ons in slowing down to rest. With charged particle irradiation, the Coulomb force between the nucleus of the stationary atom and the charged particle is largely responsible for producing the primary knock-ons. For sufficiently high energy radiation, the collisions are ordinary unscreened Rutherford collisions; in an intermediate range of energies, the simple Coulomb interaction has to be modified to allow for the screening effect of the extra-nuclear electrons; and at the lowest energies the Coulomb forces and the screening electrons produce, to a first approximation, hard sphere interaction. In many cases, the collisions made by the primary knock-ons come into this last category. Fast neutron bombardment produces primary knock-ons by nuclear collisions. The displaced atoms which have been detected in γ -irradiated metals are thought to be produced by Compton electrons.

It is insufficient in most cases to suppose that the defects formed are randomly distributed interstitial atoms and vacancies. The majority of the displaced atoms cannot move more than a few interatomic distances from their original lattice sites before coming to rest. Also, the defects are often concentrated into small volumes; in some cases this grouping is so marked that the production of the defects is probably best thought of as a consequence of rapid melting and solidification of the small volume.

For most room temperature irradiations, some recovery takes place during and immediately after irradiation. This must usually be the recombination of close pairs of interstitials and vacancies, and it occurs however low the dose. Consequently the temperature of irradiation not only controls the ultimate concentration of defects obtainable at high doses, but also affects the rate of accumulation of defects at low doses. Also, the recovery reactions often have a high effective order of reaction, so that although some recovery may occur within a few hours, all the effects may be removed only when the temperature of the specimen is raised.

Experimental studies of the effects in metals have mainly used low temperature irradiations, since at room temperature recovery is so marked that only small effects, and sometimes none, can be detected; copper, for instance, shows marked recovery at 40°K. The process of displacement and recovery can, however, produce disorder in an ordered alloy at room temperature, as has been observed in several instances. The electrical resistivity of metals is increased by irradiation because the electron mean free paths are reduced by the defects, and it provides an easily measured parameter that has been much used for studying irradiation and recovery processes. Activation energies of the recovery processes have been measured and compared with activation energies obtained from calculations or observed in other processes. The simple recombination of interstitials and vacancies is not adequate to explain all the stages of recovery observed in the resistivity of metals, and more complicated defects must be formed. There is as yet no real evidence for the nature of these defects. This is particularly true of the stage associated with the recovery of the increase of yield stress caused by irradiation.

The electrical properties of semiconductors, which change dramatically at quite low doses, have been extensively studied. In this case, the changes arise from the trapping of charge carriers at the defects. In graphite, which has properties intermediate between a metal and a semiconductor, the changes of electrical resistance arise both from mean free path changes and also from trapping of charge carriers.

In insulators, thermal conductivity at low temperatures is very sensitive to defects; moreover, by measuring the thermal conductivity at different temperatures it has been possible to distinguish between isolated defects of atomic dimensions, and large groups of defects which give phonon scattering analogous to boundary scattering. X-ray measurements have shown that lattice expansion is a characteristic irradiation effect, and there is a rough correlation between the expansion and the proportion of interstitial atoms. Measurable damage to the lattice periodicity sometimes accompanies the expansion. In most covalent compounds the defects appear to be more stable than in metals, for measurable effects are easily obtained at room temperature, and sometimes heating at 1000°C fails to produce complete recovery. In many cases it seems that the end product of prolonged bombardment is a saturation concentration of Frenkel defects of not more than about 1% in the original crystal lattice. In certain cases, however, the crystal structure is broken down, and the end product is a glassy amorphous state known for many years to mineralogists as the metamict state. Many radioactive minerals, which have had very large irradiation doses, are found in this state, though they retain a relatively perfect outward morphology, and can be restored to a crystalline state by heating at high temperatures. It is not understood why the metamict state appears in some materials and not in others.

§ 1. INTRODUCTION

1.1. *General*

WHEN solids are bombarded with radiation, electrons may be removed from their normal orbits, and atoms may be knocked out of their normal sites. Further, impurities may be introduced, either by nuclear transmutations or by bombarding ions coming to rest in the material. As a result, the irradiation of solids is apt to change their properties, sometimes slightly, sometimes drastically. Much of the current interest in these *irradiation effects* has been aroused by the need to understand and mitigate them in materials used in nuclear reactors (Wigner 1946); in this context, the effects are often referred to as *irradiation damage*. However, with the increased understanding of the role of defects in crystalline solids, considerable interest has also been aroused by the possibility of the controlled introduction of defects by irradiation, which can have valuable applications.

This article is primarily concerned with the displacement of atoms, and the consequent effects. The displacement of electrons produces effects in insulators, most notably coloration effects in alkali halides, a subject recently reviewed by Seitz (1954). Also, the displacement of electrons can produce 'displaced' atoms by breaking chemical bonds for a time long compared with the periods of thermal vibration. A striking example is the large irradiation effects observed in plastics (Sisman and Bopp 1951, Charlesby 1954). Such effects are akin to ionization induced chemical reactions and, although it is not possible to distinguish sharply between radiation chemistry and radiation damage, we shall only be concerned with the effects of displaced electrons in cases where they occur simultaneously with, or have an important bearing on the effects of the displaced atoms produced by direct momentum transfer. Likewise the introduction of foreign atoms is of secondary interest here.

1.2. *Historical*

Prior to the discovery of radioactivity, only relatively low energy radiation was available which, when capable of displacing atoms, has only a low penetrating power. Such radiation served, however, to reveal the phenomenon of sputtering (Grove 1852, Massey and Burhop 1952), the displacement of atoms from surfaces by the impact of ions, which is due essentially to the same mechanisms as those considered herein.

With the discovery of radioactivity and the isolation of sources of high specific activity, many bulk effects were observed (Rutherford, Chadwick and Ellis 1930), although most subsequent developments were concerned with their chemical aspects (Lind 1928, Hahn 1936). H. G. Wells (1909) dramatically visualized the possibility of mechanical failure of constructional materials under intense irradiation. Certain phenomena observed in minerals, the best known being the pleochroic haloes (Joly 1907) in mica and fluorspar, were accounted for by the bombardment due to radioactive elements.

As early as 1893, sufficient mineralogical data had been collected for Broegger (1893) to generalize and define *metamict* materials as originally crystalline materials which have in the course of time assumed the properties of amorphous substances. While retaining their original morphology, they have become less dense, assumed

conchoidal fracture (instead of cleavage) and become optically isotropic; some of them exhibit a sudden release of stored energy when they are heated (Berzelius 1815). All metamict crystals contain uranium or thorium, either as a normal constituent or as an impurity ($> \sim 0.1\%$), and it is now clear that as originally suggested by Hamberg (1914), the metamict state is brought about by the bombardment of the α -particles and recoil nuclei produced in the radioactive decay of uranium and thorium. An admirable summary of present-day information on the metamict state has been given by Pabst (1952), and this, together with results published subsequently, makes it clear that an important part of the available observations on irradiation effects have been made on metamict minerals.

Since the development of nuclear reactors much progress has been made in understanding irradiation effects. Burton (1947), Slater (1951), Seitz (1949, 1952 a), Broom (1954), and Koehler and Seitz (1954) have discussed various aspects of the phenomena encountered. Dienes (1953 a b) has reviewed the experiments reported prior to March 1952. We endeavour in the present article, by using both the mineralogical data and the many results that have become available since 1952, to give a more detailed account than hitherto of the mechanisms involved.

1.3. *Relation between Theory and Experiment*

Very diverse phenomena are produced in solids by irradiation. Partly this is because the changes produced by irradiation are usually metastable; they depend critically on the structure of the solids, the nature of the interstitial sites available for the displaced atoms, the height of potential barriers, and suchlike detailed properties. Also some recovery usually occurs during or just after irradiation, and the magnitude of the effects is often very sensitive to temperature both of irradiation and of observation. Further, the subject is in a relatively early stage of development, so that at present a great many of the conclusions drawn await confirmation.

Consequently there is no simple set of rules, or basic theory to guide studies in this field. Instead, the possible processes taking place must be conjectured theoretically, and the experimental data in any instance must be analysed to find a combination of likely processes which fits the facts. These theoretical considerations of the number and grouping of the displaced atoms produced by irradiation, and of their recovery, are the main concern of § 2 and § 3.

§ 2 THE PRODUCTION OF DISPLACED ATOMS

2.1. *Energy Considerations*

2.1.1. *Displacement energy.*

From heats of sublimation and similar thermodynamic data, it is known that atoms are bound in solids with energies which are generally about 5 eV; it must be expected that more energy is needed to displace an atom from a lattice site within the solid. Firstly, more bonds are broken in displacing an atom inside a solid than in evaporating one from the surface; secondly, there must be a potential barrier between the lattice site and a stable interstitial site. Results of a detailed calculation for the case of copper have been given by Huntington (1954), who finds that the energy required depends on the direction (with respect to the

crystal axes) in which the displaced atom is knocked, and lies between 18 and 43 ev.

Experimental data from threshold energies for irradiation effects yield 31 ev for germanium (Klontz and Lark-Horovitz 1951), 25 ev for copper (Eggen and Laubenstein 1953), <12 ev for copper atoms in Cu₃Au (Dugdale 1955) and ≥25 ev for iron in iron-copper alloy (Denney 1953). Threshold energies for sputtering are neither very reliable for application to irradiation damage, nor easy to obtain experimentally. They will, however, give an order of magnitude. Values ranging from 20 ev for Pb to 180 ev for Hf have recently been found in 23 metals by Werner (1954).

Since the displacement energy varies with direction of recoil, must vary from one material to another, and cannot be at all easily calculated, the easiest practical procedure is to follow Seitz (1949) in taking an isotropic value of 25 ev, and to modify this value only when directly indicated by experiment. This has generally been done in work so far published.

2.1.2. Threshold radiation energies.

With this working value of 25 ev for the displacement energy, the minimum radiation energy for the production of displaced atoms by the various types of radiation may readily be calculated. Results are presented in table 2.1. In the

Table 2.1. Threshold Radiation Energy for Displacements with $E_d=25$ ev

Atomic weight of stationary atoms	10	50	100	200
Neutrons, protons (ev)	76	325	638	1263
Electrons, γ -rays (MeV)	0.10	0.41	0.68	1.10
α -particles (ev)	31	91	169	325
Fission fragments (ev)	85	30	25	27

case of massive-particle radiation, the expression for the maximum energy E_{\max} transferred by moving particle of mass M_1 and energy E to a stationary atom of mass M_2 ,

$$E_{\max} = AE \quad \dots\dots(2.1)$$

$$\text{where} \quad A = 4M_1M_2/(M_1 + M_2)^2 \quad \dots\dots(2.1a)$$

has been used. For electron bombardment, relativistic effects are important, and we have used the expression

$$E_{\max} = 2E(E + 2mc^2)/M_2c^2 \quad \dots\dots(2.2)$$

where m is the electron mass, and c is the velocity of light. In the case of γ -rays, the threshold energy is determined by the energy of the photo- or Compton electrons, and therefore is the same roughly as the threshold for electrons. Direct interaction of γ -rays with the nucleus is rarely important except in the case of nuclear recoils from γ -emission, as in the Szilard-Chalmers process (McKay 1950).

2.2. The Number of Displaced Atoms

Atoms which are displaced by direct collisions with the bombarding radiation we call 'primary knock-ons', to distinguish them from those atoms displaced as a consequence of the subsequent collisions of the primary knock-ons. In §§ 2.2.1–2.2.4, we deal generally with the collisions of moving atoms, and obtain expressions

both for the number of displaced atoms produced by a primary knock-on, and also for the cross sections for the production of primary knock-ons by bombarding ions. We use these expressions to calculate the total number of displaced atoms for certain cases, and in later sections, for the case of neutrons, electrons and γ -ray bombardment.

No accurate experimental determinations of numbers of displaced atoms are available, but some rough estimates provide comparisons between calculated and observed numbers, which we give in table 2.2. The calculated number is usually the greater of the two, probably because of the occurrence of recovery. In each

Table 2.2. Ratio of Calculated to Observed Numbers of Displaced Atoms

Material	Radiation	Calc. no. Obs. no.	Assumptions
Copper	10 mev deuterons	3	Electrical resistivity increased by $2\mu\Omega$ cm for 1% Frenkel defects
Silver	" " "	4	
Gold	" " "	4	
Germanium	1.5 Mev electrons	2	2 electrons trapped per Frenkel defect
Quartz	Fast neutrons	5	3% density change for 1% Frenkel defects
Boron nitride	Li and α -particles	> 5	x-ray intensity changes detectable for > 1% Frenkel defects.

case the experimental estimate depends on some sort of assumption relating the effects observed to the number of displaced atoms. These assumptions are briefly indicated in table 2.2; further details are given in § 5.

2.2.1. *Moving atoms: principles.*

Calculations for moving atoms have been made by Seitz (1949), Ozeroff (1949) and Brinkman (1954). Although the majority of Seitz's results are correct, his treatment is based on the use of the Born approximation, which is invalid for the collisions involved. Clear discussions of the ranges of validity of the different approximations have been given by Bohr (1948) and Williams (1945), and for all the collisions of interest herein, the classical approximation must be used. Ozeroff deals primarily with the case of atoms displaced by fission fragments. Brinkman, who corrects an error in Ozeroff's working, deals with the case of identical moving and stationary atoms, but does not explicitly calculate the number of displaced atoms. We base our discussion on the work of Knipp and Teller (1941) and Bohr (1948).

Our basic approximation is that the atoms are displaced by the Coulomb interaction between the nuclei, and that the effect of the screening electrons is to cut off this interaction sharply at a radius of about $a_0/Z^{1/3}$, where a_0 is the Bohr radius and Z is the atomic number. When the kinetic energy of the moving atom is less than the Coulomb interaction potential of the two nuclei separated by the radius of the screening electron cloud, the screen produces hard sphere collisions. The upper energy limit L_A for the validity of this approximation is (Bohr 1948)

$$L_A = 2E_R Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2} (M_1 + M_2) / M_2 \quad \dots\dots(2.3)$$

where E_R is the Rydberg energy (13.60 ev), Z and M are atomic numbers and masses respectively, and the subscripts 1 and 2 refer to moving and stationary atoms respectively. At energies above L_A the effect of the screening electron

clouds is to cut off the Rutherford collisions at impact parameters of $a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2}$ and the minimum energy E^* that can be transferred is given by

$$E^* = 4E_R^2 Z_1^2 Z_2^2 (Z_1^{2/3} + Z_2^{2/3}) M_1 / M_2 E. \quad \dots\dots(2.4)$$

As long as E^* is more than the displacement energy E_d all Rutherford collisions displace atoms; but when the energy E of the moving atoms exceeds L_B where

$$L_B = 4E_R^2 Z_1^2 Z_2^2 (Z_1^{2/3} + Z_2^{2/3}) M_1 / M_2 E_d \quad \dots\dots(2.5)$$

only some of the Rutherford collisions do so. When $E \gg L_B$, it is easily shown that half the energy lost in Rutherford collisions is dissipated in lattice vibrations without displacing atoms.

The remaining interaction of importance is electronic excitation. Following Seitz (1949), we assume that energy loss from this source exceeds all others by a large factor ($\sim 10^3$) when $E > L_C$, and is zero when $E < L_C$; L_C is determined by the lowest excitation potential I_t of the valence electrons, and is roughly given in insulators by

$$L_C = (M_1/m) I_t / 8 \quad \dots\dots(2.6a)$$

where I_t is a well-defined value corresponding to the edge of the first main optical absorption band. In metals, where the valence electrons are free, electronic excitation losses occur at all energies. Ozeroff shows that at sufficiently low energies, these losses can be neglected in comparison with collision losses. No satisfactory criterion has been given for the energy above which electronic losses predominate, Seitz's expressions being invalid owing to his use of the Born approximation. Clearly, however, once the velocity of the moving atom is much less than that of electrons at the top of the Fermi distribution, only a small proportion of the electrons can be excited, and we take, by rough analogy with the case of insulators,

$$L_C = \frac{1}{16} \frac{M_1}{m} \epsilon_0 \simeq \frac{1}{16} \frac{M_1}{m} \pi a_0^2 E_R (3N_0 \sqrt{\pi})^{2/3} \quad \dots\dots(2.6b)$$

where ϵ_0 is the Fermi energy of the free electrons, and N_0 is the number of atoms per unit volume.

With heavy moving atoms, the assumption of a sharp cut-off to the ionization losses is very crude, owing to the large change in the effective charge of the moving atoms. Knipp and Teller (1941) show that ionization losses and collision losses are of about the same magnitude over quite a wide range of energy. Our values of L_C represent energy limits *below* which ionization losses may be neglected. We give some values of L_A , L_B and L_C in table 2.3.

Table 2.3. Energy Limits for Collision Processes

Substance	Moving Atom	Energy Limits (ev)		
		L_A	L_B	L_C
Diamond	Carbon	5×10^3	3×10^3	$1.5 \times 10^4 a$
Diamond	Deuteron	4×10^2	8×10^2	$2 \times 10^3 a$
Aluminium	Aluminium	3×10^4	9×10^6	1.7×10^4
Aluminium	Deuteron	1×10^3	2×10^3	1.3×10^3
KCl	Argon	6×10^4	4×10^7	$7 \times 10^4 b$
KCl	Deuteron	1.4×10^3	4×10^3	$3 \times 10^3 b$
Copper	Copper	2×10^5	4×10^8	5×10^4
Copper	Deuteron	3×10^3	8×10^3	1.6×10^3
Gold	Gold	2×10^6	4×10^{10}	1.2×10^5
Gold	Deuteron	1×10^4	4×10^4	1.2×10^3

The value of the first excitation level of the valence electrons is taken from: a, Moss (1952), b, Schneider and O'Bryan (1937).

2.2.2. Moving atoms: hard sphere collisions.

The essential feature of hard sphere collisions is that the probability of transferring a given energy ΔE , is independent of ΔE for $0 \leq \Delta E \leq \bar{E}$ and is zero outside this range. Consider a monatomic solid in which a primary knock-on of energy \bar{E} has been produced. At its first collision the energy is shared by two atoms and at the second group of collisions the energy is shared by four atoms. Likewise, after the p th group of collisions the energy is shared by 2^p atoms and the number of atoms in an energy range dE is found to be

$$N_p(E)dE = 2^p (\ln(\bar{E}/E))^{p-1} dE/\bar{E}(p-1)! \quad \dots\dots(2.7)$$

This result applies to free stationary atoms; but only those which receive more than the threshold energy E_d are displaced. Further, only an atom with energy greater than $2E_d$ can make a collision with a stationary atom, after which both have energy exceeding E_d . Thus we assume that atoms with energies between E_d and $2E_d$ are displaced but cannot themselves further increase the total number of displaced atoms. The number of such atoms produced by the p th group of collisions may be shown to be $E_d N_p(2E_d)$, so that the total number N_d of displaced atoms is

$$N_d = \sum_{p=1}^{p=\infty} E_d N_p(2E_d) = \bar{E}/2E_d. \quad \dots\dots(2.8a)$$

This is valid only for $\bar{E} > 2E_d$; obviously for $0 \leq \bar{E} \leq 2E_d$,

$$N_d = 1. \quad \dots\dots(2.8b)$$

Since (2.8a) is linear in \bar{E} it is also correct when \bar{E} represents the average energy of a group of primary knock-ons with energy greater than $2E_d$. It is easily shown that (2.8a) is also valid when the mass of the initial moving atom is different from that of the stationary atoms, provided $2E_d/\bar{E} \ll 1$.

A simple argument due to T. M. Fry also leads to (2.8a). A net increase in the number of displaced atoms can be produced only when a moving atom with energy greater than $2E_d$ collides with a stationary atom. At such collisions, atoms appear in the energy range $0-2E_d$ with uniform energy distribution and average energy E_d . The number of atoms which become involved in such collisions is therefore \bar{E}/E_d ; consequently the number of displaced atoms is $\bar{E}/2E_d$.

The physical assumptions in the derivation of equation (2.8a) are such that it probably represents an overestimate of the number of displaced atoms. Seitz states that the formula

$$N_d = (E'/E_d)^{1/2} \quad \dots\dots(2.9)$$

where E' is the average energy of *all* the primary knock-ons, is a good approximation when E' is a few times E_d . Comparison with equations (2.8a) and (2.8b) show that agreement is reasonable up to $\bar{E} \sim 10E_d$. Ozeroff gives an approximate treatment based on the Thomas-Fermi model, which allows for the electrostatic interaction of the screening electron clouds. His results, which cannot be presented in a simple analytical form, give values of N_d some 30% less than equation (2.8a). The calculations contain the error pointed out by Brinkman and some imperfectly justified assumptions; the results can therefore be used only as a rough guide to the accuracy of equation (2.8a).

2.2.3. Moving atoms: Rutherford collisions.

When $E > L_B$ the cross section σ_p for a Rutherford collision in which energy greater than E_d is transferred is readily found, by applying the ordinary theory for unscreened nuclei (Bohr 1948), to be

$$\sigma_p = 4M_1Z_1^2Z_2^2E_R^2(1 - E_d/AE)\pi a_0^2/M_2E_dE. \quad \dots\dots(2.10)$$

The symbols are defined in § 2.2.1; πa_0^2 has the value $8.8 \times 10^{-17} \text{cm}^2$. The term $(1 - E_d/AE)$ is very close to unity for all cases of interest, and may be omitted, so that the cross section increases as the energy of the moving atom decreases. It follows from equation (2.10) that the number of primary knock-ons varies inversely as the square of their energy, and their mean energy \bar{E} is given by

$$\bar{E} = E_d \ln(AE/E_d). \quad \dots\dots(2.11)$$

As Seitz points out, the logarithmic term is insensitive to the exact values of A and E , and \bar{E} is between 3 and 15 times E_d for most practical cases. At such energies the hard sphere results may be used to calculate the number of atoms displaced by the primary knock-ons. From equations (2.8a) and (2.8b) the average *total* number N_d of displaced atoms produced for every primary knock-on is

$$N_d = \frac{1}{2} \{ 1 + \ln(AE/2E_d) \}. \quad \dots\dots(2.12)$$

These equations may be applied directly to such cases as the cyclotron irradiation of thin foils; for copper irradiated with 10 mev deuterons, we obtain $\sigma_p = 6900$ barns, $\bar{E} = 2700$ ev and $N_d = 5.8$.

When $L_A < E < L_B$, as in the case of fission fragments and energetic primary knock-ons, all the Rutherford collisions produce displaced atoms, and σ_p is approximately constant and equal to $\pi a_0^2/(Z_1^{2/3} + Z_2^{2/3})$. The average energy of the primary knock-ons and N_d can be estimated by replacing E_d by E^* in equation (2.11).

Both Brinkman and Ozeroff refine our approximation of a sharp cut-off of the nuclear interaction, by considering the energy transfer between two Thomas-Fermi atoms with rigid charge distributions. Brinkman gives an expression of σ_p for the case $Z_1 = Z_2$ valid at all energies which confirms the condition $E > L_B$ for equation (2.10), and which shows the expected slow variation of σ_p with E when $E < L_B$. Ozeroff's approximate results show that the nuclear Rutherford collisions are the predominant source of energy loss, down to energies at which the hard sphere interaction becomes dominant. Both these workers use an approximate form of the Thomas-Fermi potential, and take the radius of the screening electron cloud as $2.09a_0/Z_2^{1/3}$; Knipp and Teller give the value $0.85a_0/Z_2^{1/3}$ (assuming $Z_2 > Z_1$), and Bohr gives $a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2}$. We have used Bohr's value.

2.2.4. Moving atoms slowing down to rest.

We have already shown that the total number of displaced atoms produced when an atom of energy E slows down to rest is $E/2E_d$ when $E < L_A$. Provided $E < L_C$ this result also holds for $L_A < E < L_B$, since the predominant energy loss in this range is then due to Rutherford collisions which produce primary knock-ons (see also Snyder and Neufeld 1954). When $E > L_B$ only some of the energy is expended in this way, and the result no longer holds; for the case $E \gg L_B$ the total number of displaced atoms is approximately $E/4E_d$.

Usually, however, when $E > L_B$, E is also greater than L_C and electronic

excitation losses have to be taken into account. In the high energy case of $E \gg L_C$, $E \gg L_B$, these losses, which predominate, are given by

$$-(dE/dx) = 2\pi(qZ_1)^2 e^4 Z_2 N_0 (M_1/mE) \ln(4Em/M_1 I) \quad \dots\dots(2.13)$$

where e is the electronic charge, N_0 is the number of atoms per unit volume, I is a mean ionization potential of the stationary atoms, and qZ_1 is the effective charge of the moving atom. Full discussions of equation (2.13) and the appropriate values of I and q are given by Bethe and Ashkin (1953) and by Allison and Warshaw (1953). Combining equations (2.13), (2.10) and (2.12), it is found that in losing energy ΔE , a moving atom displaces ΔN_t atoms where

$$\Delta N_t = P \Delta E / E_d \quad \dots\dots(2.14)$$

and

$$P = mZ_2 \{ 1 + \ln(\Delta E / 2E_d) \} / 4M_2 q^2 \ln(4Em/M_1 I). \quad \dots\dots(2.14a)$$

When $q \simeq 1$, P is usually between 10^{-3} and 10^{-4} .

For very light moving atoms such as α -particles produced by radioactive disintegrations, q and I are constant over a large proportion of the energy range, and P is so insensitive to E that a mean value can be used without serious error. Furthermore, the energy range $L_B - L_C$ is small, and equation (2.14) can be applied with a constant mean value of P to all energies in excess of L_C . Thus the total number N_t of displaced atoms produced by a very light moving atom of energy E_0 in slowing down to rest is

$$N_t = \{ P(E_0 - L_C) + bL_C \} / E_d \quad \dots\dots(2.15)$$

where P is given by equation (2.14a), L_C is given by equation (2.6), and b is $\frac{1}{2}$ if $L_B > L_C$ and $\frac{1}{4}$ if $L_B \leq L_C$. Essentially the same result is obtained by Seitz. In cases where the term bL_C predominates, a great deal of uncertainty is introduced by the procedure for obtaining L_C , which is hardly more than qualitative.

The case of heavy moving atoms with $E > L_C$ is more complex because ionization losses are predominantly governed by variations in the effective charge. Also L_B is usually so large that equation (2.10) no longer applies over a large energy range, if at all. This case is dealt with in detail by Ozeroff. Essentially, equation (2.13) is replaced by a semi-empirical expression, E_d is replaced by E^* in equation (2.11) and a series of averages is taken to circumvent the mathematical complexities. This procedure is essential in the case of fission fragments. For the case of fast-moving primary knock-ons, the initial energy is not often greatly in excess of L_C , and it is often sufficient to suppose that *all* the excess energy is expended in ionization losses, so that the number of atoms displaced is $L_C / 2E_d$.

2.2.5. Fast neutrons.

The fast neutrons used in irradiation work are usually produced by fission. Watt (1952) gives an energy spectrum, having a maximum at 0.7 mev and a mean energy of 2 mev, for fission neutrons from both ^{235}U and ^{239}Pu .

The collisions of the neutrons are of the simple hard-sphere type, and so the recoil energy spectrum $N(E)dE$, of the struck atoms is given by

$$N(E)dE = dE/E_{\max} (0 \leq E \leq E_{\max}) \quad \dots\dots(2.16)$$

where E_{\max} is given by equation (2.1). Only the negligible proportion E_d/E_{\max} of the struck atoms are not displaced, so that σ_p , the cross section for producing a

primary knock-on is the total neutron cross section. For the heavy elements, E_{\max} does not usually exceed the ionization limit L_C . Applying the results of the previous sections, the total number N_d displaced on the average for each fast neutron collision is given by

$$N_d = E_{\max}/4E_d. \quad \dots\dots(2.17)$$

For lighter elements E_{\max} generally exceeds L_C , but except for very light elements, the primary knock-ons effectively lose *all* the excess energy in ionization, and in this case

$$N_d = (2 - L_C/E_{\max})L_C/4E_d. \quad \dots\dots(2.18)$$

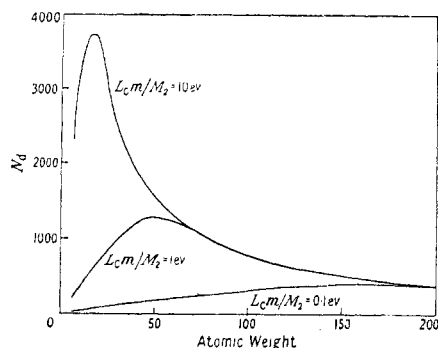


Figure 2.1. The average number of displaced atoms per primary knock-on produced by 2 mev neutron bombardment as a function of atomic weight.

Values of N_d for 2 mev neutrons are presented at figure 2.1, for various values of the parameter $L_C m/M_2$. This parameter is not a sharply varying function of M_2 , and is of the order of 1 ev in many materials. The shape of the curves shows that 2 mev neutrons produce the maximum number of displacements for moderately heavy elements. Heavy nuclei take up less recoil energy; lighter nuclei receive more energy but lose a greater proportion in ionization (Burton 1947).

Ozeroff (1949) has applied his more complex expressions, referred to in § 2.2.3, to the number of atoms displaced by fast neutrons, and both he and Seitz give some values for the case of a fast neutron slowing down to rest.

2.2.6. Electrons.

Electrons displace atoms by Coulomb interaction with the nuclei. They invariably have to penetrate the K electron shells to do so, and therefore expressions derived on the basis of an unscreened Coulomb field can safely be used. However, we cannot use equation (2.10) because the electrons normally have relativistic velocities. The relativistic expression of Mott (1929, 1932) for the differential scattering cross section forms the basis of the calculation. This expression cannot be put into a rigorous explicit form. Dugdale and Green (1954), using the α^2 approximation of McKinley and Feshbach (1948), obtain

$$\sigma_p = \frac{4Z^2 E_R^2 E_{\max}}{m^2 c^4 E_d} \frac{1 - \beta^2}{\beta^4} \times \left[1 + 2\pi\alpha\beta \left(\frac{E_d}{E_{\max}} \right)^{1/2} - \frac{E_d}{E_{\max}} \left\{ 1 + 2\pi\alpha\beta + (\beta^2 + \pi\alpha\beta) \ln \left(\frac{E_{\max}}{E_d} \right) \right\} \right] \pi a_0^2 \quad \dots\dots(2.19)$$

where E_{\max} is given by equation (2.2), β is the electron velocity divided by the velocity of light, and $\alpha = Z_2/137$. McKinley and Feshbach estimate that their α^2 approximation is satisfactory when $Z \leq 27$ and $\beta \simeq 1$; for the calculation of σ_p , equation (2.19) is probably adequate well outside these limits. Klontz (1952) and Denney (1954 a) give essentially similar expressions based on Mott's own approximation; there are some discrepancies which can be rectified with the aid of Bethe and Ashkin (1953, p. 280).

The variation of σ_p with electron energies is shown in typical cases in figure 2.2. For small values of β , equation (2.19) reduces to (2.10). For electrons, the variation of σ_p with energy is predominantly due to the term $1 - E_d/\Delta E$, since $\Delta E \sim E_d$, whereas for ions, this term is negligible. Thus in contrast with ions, σ_p for electrons increases with energy in the range of practical interest. Moreover, the

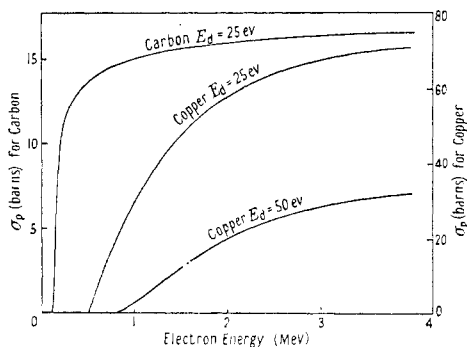


Figure 2.2. Cross section for producing primary knock-ons by electron bombardment as a function of energy.

relativistic factors usually intervene before any decrease similar to that of equation (2.10) can be observed. At high energies $M_2 c^2 \gg E \gg mc^2$, $E_{\max} \gg E_d$ the cross section saturates at a value given by

$$\sigma_p = \frac{8E_R^2 Z_2^2}{M_2 c^2 E_d} \pi \alpha^2_0. \quad \dots\dots(2.20)$$

To a first approximation, the number of primary knock-ons varies as the inverse square of their energy, and their mean energy is given by the equivalent of equation (2.11),

$$\bar{E} = \frac{E_d E_{\max}}{E_{\max} - E_d} \ln \left(\frac{E_{\max}}{E_d} \right). \quad \dots\dots(2.21)$$

In many cases, E_{\max} is no more than a few times E_d —for instance in copper it is 68 eV for 1 MeV electrons—and the total number of displaced atoms is not greatly in excess of the number of primary knock-ons.

Denney (1954 a) has shown that recoil energy taken up by bremsstrahlung represents only a small correction, and has also integrated σ_p over the range of the electrons.

2.2.7. Gamma rays.

The production of displaced atoms by γ -rays has received very little attention so far. However, Dugdale (1955) has shown that measurable effects can be produced. Most of the results required for obtaining cross sections are given by Bethe and Ashkin (1953). For γ -ray energies of about 2 MeV and materials with

$Z_2 \lesssim 50$ the predominant interaction is the Compton effect. Atoms are displaced by the recoil Compton electrons. For the case of copper irradiated with 5 mev γ -rays, σ_p is about 0.1 barn.

For heavy elements the direct displacement of the atoms by recoil from the photoelectric effect is predominant. The cross section σ_K for photoelectric absorption (for $E \gg mc^2$) is approximately

$$\sigma_K = Z_2 \alpha^4 (mc^2/E) \exp \{ -\pi\alpha + 2\alpha^2(1 - \ln\alpha) \} \text{ barns.} \quad \dots\dots(2.22)$$

$\alpha = Z_2/(137)$. For 5 mev γ -rays, this gives cross sections of the order of 10^{-24} cm² for the very heavy elements. Not every photoelectric absorption will displace the atom concerned, since the distribution of the emitted electrons with respect to the incoming γ -ray has to be taken account of, and σ_K is likely to be an overestimate for σ_p .

None of the other γ -ray processes would appear to be as important at these energies as the two we have discussed. At rather higher energies (≥ 10 mev, depending on Z_2), pair production is the predominant γ -ray process, and it must be expected that atoms will be displaced by recoiling electrons and positrons, and by the recoil of the nuclei involved in the pair-production.

2.3. Distribution of Displaced Atoms and Vacancies

2.3.1. Collision models.

In all cases, the *majority* of the displaced atoms leave their lattice sites with energies of no more than two or three times E_d . At these energies, a moving displaced atom will make a collision roughly every mean interatomic distance travelled, and will lose half its energy on the average at each collision. If we suppose that it becomes trapped in an interstitial site when it is slowed down to 1 ev, a displaced atom will usually have made no more than six or seven collisions before being trapped, and will thus be only a few interatomic distances away from the vacancy left behind.

The simplest case is provided by electron or γ -ray bombardment when the primary knock-ons have insufficient energy to displace further atoms. The radiation damage consists of a random distribution of Frenkel defects in which the distance between the interstitial and the vacancy can rarely be more than four or five interatomic distances. When the electrons can impart more than $2E_d$ to the primary knock-ons, these will displace further atoms, and some of the single Frenkel defects will become groups of two or more interstitial atoms together with the corresponding vacancies, all within a few interatomic distances of each other.

In the case of a fast-moving atom, along the first part of the track where $E > L_B$ and equations (2.10) and (2.11) are valid, the damage consists of groups of several vacancies and interstitial atoms, widely separated along the track of the ion. As the atom slows down, the cross section for producing primary knock-ons increases and the groups become more frequent; when $E \ll L_B$ a primary knock-on is produced for roughly every interatomic distance travelled (Brinkman 1954), and so the concentration of interstitials and vacancies is very high at the end of the track. This feature of irradiation damage has been found experimentally by Brattain and Pearson (1950) and by Meyer (1954). It is also a characteristic feature of the pleochroic haloes observed in mica, where the best defined haloes are shells of metamict material (Hurley and Fairbairn 1953).

Fast neutron bombardment must usually produce the highly concentrated type of damage last mentioned. When the energy of a knock-on atom is sufficiently low, the mean free path between collisions in which a large fraction of the energy is lost approaches the interatomic distance. Under these conditions, the collision models suggest that the damage will consist of a region containing a very high concentration of vacancies, surrounded by a region with a high concentration of interstitial atoms.

2.3.2. 'Displacement spikes' and 'thermal spikes'.

Brinkman (1954) has suggested that with the highly concentrated damage obtained with fast neutron bombardment of heavy elements, it is pointless to speak of individual collisions and has proposed that the volume affected is melted for a short period, and then solidifies, in the main with the same crystallographic orientation as the parent material. Such volumes he calls *displacement spikes*. The size of the displacement spike is determined as follows. As a moving atom slows down, the cross section for displacement collisions increases; at the point where one displacement collision occurs for every interatomic distance travelled, *all* the remaining energy of the moving atom is distributed in a displacement spike with an average energy of 1 ev per atom. The average size of a displacement spike produced by 2 mev neutrons in copper is thus estimated to be 75 Å in diameter, and contains 2×10^4 atoms.

Brinkman suggests that the main defects introduced by such spikes would be small dislocation loops, and a small number of interstitial atoms and vacancies quenched in on solidification.

A rather similar model—the *thermal spike* model—has been proposed by Seitz (1949), in which a moving particle heats up the material surrounding its track through the solid for times of the order of 10^{-12} second. As in the case of displacement spikes, the consequences of the rapid heating and cooling cannot be predicted at all clearly (Koehler and Seitz 1954). Experimentally, it is observed that the ordered alloy Cu_3Au is disordered by neutron bombardment more rapidly than would be expected simply from the number of atoms displaced, and this is consistent with the displacement spike model.

The practical validity of these models depends on the limits of volume and time to which the macroscopic concepts of heat can be applied. The frequencies of atomic vibrations are in the range 10^{12} – 10^{13} sec^{-1} . During a time of 10^{-12} second, a disturbance to the lattice is propagated by elastic waves for distances of between 10 and 50 Å, which is also about the mean free path of phonons in insulators at room temperature (Kittel 1953, p. 82). Consequently, in insulators, it is unsafe to apply the macroscopic concepts of heat for times shorter than 10^{-12} second, or to volumes with linear dimensions much less than 50 Å. In metals, where free electrons play a dominant role in the transport of energy, elastic disturbances are mainly converted to disturbances of the free electrons in times of about 10^{-13} second (Kittel 1953, p. 243). The mean free path associated with the transport of energy by free electrons is of the order of 100 Å or more, and so a rather larger volume is probably necessary in metals than in insulators before the macroscopic concepts of heat can be applied.

With these rather rough criteria, it can be seen, for instance, that the thermal spike model of the damage produced by a fission fragment moving in uranium is probably valid. A 100 mev fragment has a range of about 4×10^4 cm (Ozeroff 1949);

it is easily shown that a cylindrical volume of 100 Å radius enclosing the track is heated to about 4000°C by the dissipation of 100 mev. Classical heat-conduction expressions show that the temperature on the track falls to half this value in about 10^{-11} second. In contrast, similar calculations suggest that the damage produced by electrons, γ -rays and energetic ($E > L_B$) light ions is probably best regarded as being produced by individual collisions.

The damage produced by neutrons is usually of an intermediate character and the criteria are too ill-defined to provide a decision. Experimentally there is no doubt that fast neutrons produce interstitial atoms, but at present it is not clear whether these are best regarded as being produced by rapid cooling of small volumes, or by individual collisions. It is quite possible that both models should be used simultaneously, for the primary knock-ons have all energies from E_d to E_{\max} , and the low energy knock-ons are almost certainly regarded best on the collision model. For general pile irradiations, because of the shape of the energy distribution of the fast neutrons (equation (4.1)) the majority of primary knock-ons have relatively low energies. Evidence that fast neutron damage can be regarded as a mixture of isolated interstitials and relatively larger volumes of concentrated damage is provided by Berman (1951) and Klemens (1951) in studies on quartz.

The same difficulty of approach has been found in attempts to account quantitatively for sputtering, and Bradley (1954) concludes that no single model so far used gives an adequate account under all conditions. He finds, however, no evidence in favour of a 'hot-spot' model for ions of energies up to 1800 ev, incident on alkali metals. The most explicit application of the 'hot-spot' model, that of Townes (1944) is open to the objection that the macroscopic concepts of heat cannot be applied to volumes containing only a few atoms for times of about 10^{-16} second. Keywell (1952) has applied a hard-sphere collision model to the sputtering caused by argon ions with energies of up to 5000 ev in silver and other metals, and obtains quite a good agreement with his observations, assuming that one silver atom is sputtered for every collision made by the argon ion in slowing down to 39 ev.

2.4. Effects in Compounds

2.4.1. Replacement collisions.

Some of the collisions between moving atoms and stationary atoms at lattice sites will displace the initially stationary atom, but leave the original moving atom with insufficient energy to escape from the vacancy thus created. Such collisions may be called replacement collisions, since they change the identity of the displaced atoms but not the total number. Replacement collisions are clearly of little consequence in monatomic solids, but in compounds they may be important.

It has been proposed (Kinchin and Pease 1955) that a replacement collision takes place when a moving atom is left with energy that is both less than E_d and less than the energy given to the stationary atom. It is further assumed that a replacement collision can only occur when the energy imparted to the stationary atom exceeds some threshold value E_p . An approximate calculation of N_p , the number of replacement collisions, for the case of neutron bombardment, based on hard-sphere collisions and assuming all the atoms have the same mass, leads to

$$N_p = 0.5 N_d [1 + \ln(E_d/E_p)/\ln(4/3)] \quad \dots\dots(2.23)$$

where N_d , the number of displaced atoms, is given by equation (2.17). Since E_p is likely to be appreciably less than E_d , the replacement collisions may well outnumber the displacement ones. This is particularly so in the case of ordered alloys, where E_p may be not much greater than the activation energy for interstitialcy diffusion which has been estimated to be about 0.25 eV (Huntington 1953) in copper.

If the masses of the atoms in a compound are very different, the number of replacements is almost certainly very much smaller than suggested by equation (2.23), for, as can be seen from equation (2.1), it is impossible for a moving atom of mass m_1 , to give up more than half its energy to an atom of mass M_2 , if A is less than a half. It is easily shown that, for replacements to occur by the mechanism proposed, $1/5.83 < M_1/M_2 < 5.83$.

2.4.2. *Disordering.*

In any compound, both replacement collisions and partial or complete recombinations of the Frenkel defects may produce atoms in lattice sites of the wrong kind. Such disordering is well known in the case of ordered alloys such as Cu_3Au and Ni_3Mn . There is little evidence available for other types of material. In the case of boron nitride, however, no disordering was detected even at very high doses (Pease 1954). Even in such a case, the irradiation must produce some defects in which a displaced atom is either in or very close to a vacant lattice site of the wrong kind. Such defects may be important in minerals, since these often contain many different kinds of atoms.

§ 3. RECOVERY

In most cases, on raising the temperature of a specimen after irradiation, the physical properties revert to their initial values. In addition, energy is released. In a few cases, after very heavy irradiation, annealing at high temperatures may cause a material to recrystallize in a new phase with a structure different from the original, as in the cases of thorite (Pabst 1952) and some forms of quartz (Wittels and Sherrill 1954). Usually one must expect some sort of recovery to take place during irradiations, at however low a temperature these are carried out.

Recovery produced by heating usually takes place in several stages, with different activation energies in different ranges of temperature, and the course of a given recovery process can usually be represented by the equation:

$$dn/dt = -cn^\gamma \exp(-\epsilon/kT) \quad \dots\dots(3.1)$$

where n is the number of defects taking part in the recovery process, ϵ is the activation energy, c is a constant and γ is often termed the 'order of reaction' by analogy with gaseous chemical reactions. This terminology is somewhat misleading, since a number of recovery processes governed by the diffusion of lattice defects give apparently high orders of reaction which are not related to the number of constituents involved, as is the case in chemical reactions.

3.1. *Recombination of Interstitials with Vacancies*

3.1.1. *Close pairs of interstitials and vacancies.*

The recombination of interstitial-vacancy pairs is discussed by Fletcher and Brown (1953). They assumed that vacancies are the more mobile defects, and

applied diffusion equations to the random migration of vacancies to spherical sinks representing interstitials. If $n(0)$ vacancies start out at a distance b from a sink of radius a in an infinite isotropic three-dimensional medium, the number, $n(t)$, remaining after a time t is given by

$$n(t) = n(0) \left\{ 1 - \frac{a}{b} + \frac{a}{b} \operatorname{erf} \left(\frac{b-a}{2(Dt)^{1/2}} \right) \right\} \quad \dots\dots(3.2)$$

where D is the diffusion coefficient for vacancies. A fraction $1-a/b$ of the vacancies is not caught by the sink, but is 'liberated' to diffuse indefinitely throughout the medium. In the early stages of 'liberation', the lattice cannot be regarded as a continuum, and Fletcher and Brown therefore used numerical solutions, applicable to the diamond lattice.

For substances with a layer structure where the diffusion of interstitial atoms (assumed to be more mobile than vacancies throughout the remainder of § 3) can only take place in two dimensions; the spherical sink of the three dimensional problem is replaced by a circular sink. The solution is:

$$n(t) = n(0) \frac{2}{\pi} \int_0^\infty \frac{\exp(-y^2 Dt)}{y} \left\{ \frac{Y_0(by)J_0(ay) - Y_0(ay)J_0(by)}{J_0^2(ay) + Y_0^2(ay)} \right\} dy \quad \dots\dots(3.3)$$

where J_0 and Y_0 are zero order Bessel functions. This equation has been evaluated by K. T. Spinney (unpublished) and some results are shown in figure 3.1. In

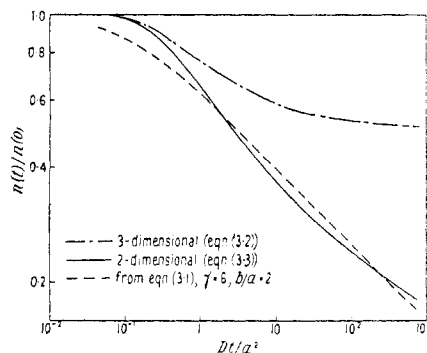


Figure 3.1. Annealing of close pairs of interstitials and vacancies.

this case there is no 'liberation' of interstitials. Equation (3.1), with $\gamma=6$, is a good approximation to equation (3.3).

3.1.2. Random distribution of interstitials and vacancies.

The combination of equal numbers of randomly distributed interstitials and vacancies follows the kinetics of a true second order reaction, i.e.

$$dn/dt = cn^2 \exp(-\epsilon/kT) \quad \dots\dots(3.4)$$

where ϵ is the activation energy for interstitial migration.

In the case of a material bombarded with electrons with energy just above the threshold energy, so that isolated Frenkel defects are produced, two stages of recovery would be expected, the first governed by equation (3.2) or (3.3) and the second by equation (3.4), with the same activation energy. The situation is complicated by the interaction between interstitials and vacancies, discussed by

Marx *et al.* (1952) and Overhauser (1953). They conclude that the lattice strain near a vacancy will reduce the activation energy for migration of a nearby interstitial and diffusion will no longer be isotropic. For short irradiations, however, the activation energy should rise during the liberation process to a value corresponding to the activation energy for migration in the undistorted lattice and the second stage should follow equation (3.4). Dienes (1953 c) has emphasized the pronounced effect of relatively small changes of activation energy on the apparent order of reaction.

3.2. Competing Processes

The recombination discussed above is too simple to explain all the observed effects. Marx *et al.* (1952) have outlined a number of other possible processes. During the annealing some interstitials may escape to dislocations or grain boundaries, thus affecting the kinetics of the interstitial-vacancy recombination. Also, after the disappearance of all the interstitials the excess of vacancies diffuse to dislocations and grain boundaries with higher activation energy. Approximate solutions for the relevant diffusion problems have been given by Fletcher and Brown (1953) and Brinkman *et al.* (1954). Groups of interstitials and of vacancies, which only dissociate with high activation energies, may also be formed.

Thus, although experimental studies of the kinetics of recovery may afford useful confirmatory evidence, they are insufficient to permit unambiguous identification of the processes. Better evidence about the recovery processes is secured by experimental measurement of well-defined activation energies, constant during comparatively large changes of the physical property measured. These can then be compared with estimates obtained from other experimental data (from cold work, quenching and self-diffusion experiments, for example) and from theoretical calculations.

3.3. Accumulation of Damage

We now consider the case of simultaneous irradiation and annealing. Irradiation generally produces groups of displaced atoms and vacancies. Provided that the interstitials diffuse for distances small compared with the distances between the groups, each group will anneal independently in the same way as the others. Hence, if dx displaced atoms are produced instantaneously by the irradiation, after a time t at a temperature T , only $dx F(T, t)$ will be left, where $F(T, t)$ is a function, independent of x , which may be determined experimentally by annealing after irradiation at very low temperatures. The total number of displaced atoms after a time t , during an irradiation in which displaced atoms are produced at the rate dx/dt' is then:

$$n(t) = \int_0^t \left(\frac{dx}{dt'} \right) F(T, t-t') dt'. \quad \dots\dots(3.5)$$

When dx/dt is constant throughout the irradiation, equation (3.5) shows that the number of displaced atoms present after a given *time* of irradiation is proportional to the flux of bombarding particles and also that, for different fluxes, the number is not determined solely by the total dose.

If the annealing of groups can be represented empirically by equation (3.1) with $\gamma > 1$ and constant activation energy, $F(T, t)$ becomes:

$$[1 + c't \exp(-\epsilon/kT)]^{1/(1-\gamma)}$$

where c' is a new constant. For $\gamma > 2$, the number of displaced atoms present after a time long compared with $(1/c') \exp(\epsilon/kT)$ is given approximately by

$$n(t) \simeq \frac{dx}{dt} \frac{\gamma-1}{\gamma-2} \left(\frac{1}{c'} \exp\left(\frac{\epsilon}{kT}\right) \right)^{1/(\gamma-1)} t^{(\gamma-2)/(\gamma-1)}. \quad \dots\dots(3.6)$$

For large values of γ the damage is almost proportional to x and the effect of simultaneous recovery is simply to reduce the apparent rate of production of displacements by the factor $\{(1/c') \exp(\epsilon/kT)\}^{1/(\gamma-1)}$. This temperature dependence of the rate of accumulation of damage, which would not be expected for low doses if the interstitials and vacancies were randomly distributed, is often observed (e.g. Marx *et al.* 1952).

3.4. Saturation

There is no term in equation (3.6) indicative of any saturation. This is because interaction between different groups of displaced atoms has been neglected. In fact, as irradiation proceeds the groups will eventually overlap and, at low temperatures when the interstitials are immobile, this will give rise to an exponential saturation of the number of displaced atoms. At higher temperatures, the approach to saturation will be governed by second order recovery.

Rather similar ideas emerge from a different approach used by Pease (1954)

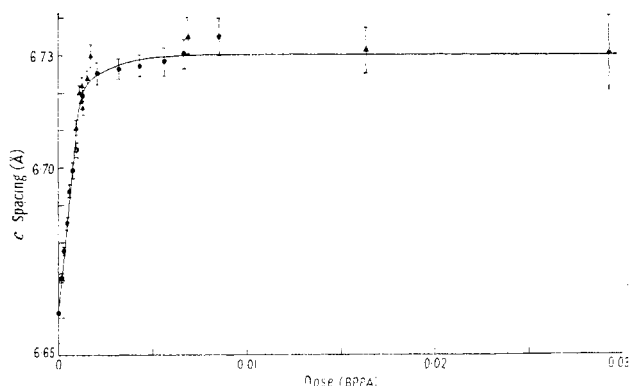


Figure 3.2. Saturation of change of lattice spacing in boron nitride. Boron nitride is a layer structure, and the c spacing is twice the interlayer spacing. The dose unit is the number of bombarding particles (α -particle and Li nuclei) per atom (Pease 1954).

in a study of saturation effects in boron nitride (figure 3.2). This used the approximation that interstitials and vacancies are stable if their separation exceeds a critical distance and that they instantly combine for smaller separations. Each interstitial atom is thus surrounded by Q lattice sites to which it can move immediately when one of them becomes vacant. Statistical arguments lead to an expression relating the concentration, y , of interstitial atoms, to the average number, p , of times each atom has been knocked into an interstitial site, which for large Q reduces to

$$y = (1/Q) \ln[2 - \exp(-pQ)]. \quad \dots\dots(3.7)$$

This expression gives $y=p$ at low doses and a saturation concentration of $y=(\ln 2)/Q$ setting in at a dose corresponding to $p \simeq 1/Q$. The effects of the temperature of

irradiation are introduced into this model by supposing that Q is temperature dependent, and that p is thus also dependent on temperature because of the marked grouping of interstitials and vacancies produced by the bombardment.

Even at the lowest temperatures, Q can hardly be less than the number of lattice sites immediately adjacent to an interstitial site, and thus the maximum concentration of interstitials which a crystalline material can support is unlikely to be much greater than 5%.

3.5. Radiation Annealing

Effects are sometimes observed which suggest that the recovery processes are hastened by the irradiation itself. Thus Cooper *et al.* (1954) observed that the rate of increase of resistivity of copper, silver and gold at 12°K decreased as irradiation proceeded, while no annealing was observed at this temperature after irradiation.

One obvious mechanism for this is the local heating produced by the passage of bombarding radiation. It seems likely, however (Koehler and Seitz 1954), that in most cases the duration of the heating is too brief to produce appreciable recovery. Koehler and Seitz suggest that the excitation of electrons facilitates the movements of interstitials or vacancies. It is also possible that collisions move the vacancies and interstitials. The threshold energy for such movements is much less than the 25 ev required for displacement and consequently the probability of moving an interstitial or a vacancy is much larger than the probability of forming it in the first place. Thus the irradiation may induce movements which are large compared with thermally activated movements, and produce a recovery which would not occur in the absence of radiation. This might appreciably reduce the saturation concentration of displaced atoms, referred to in § 3.4. This saturation may be important in limiting the concentration of displaced atoms in the groups produced by fast neutron bombardment (§ 2.3).

§ 4. EXPERIMENTAL IRRADIATION TECHNIQUES

4.1. Reactor Irradiation

4.1.1. Fast neutrons.

The radiation inside a reactor generally consists of fast and thermal neutrons, γ -rays and a small number of β -rays. The proportions of these radiations vary not only between one reactor and another, but also from one part of a reactor to another. In the majority of cases, however, the overwhelming majority of displaced atoms are produced by fast neutron bombardment.

Between the fuel rods of a graphite-moderated reactor the fast neutron energy spectrum is given roughly by the equation

$$F(E)dE = \frac{k dE}{E} \quad \dots\dots(4.1)$$

where $F(E) dE$ is a flux and k is a constant (e.g. Taylor 1952). In many cases the fast flux is approximately equal to the thermal flux. In addition, the fission neutron spectrum is superimposed in a proportion which depends on the exact position with respect to the fuel rods. Inside a hollow uranium cylinder, the damage is predominantly due to fission neutrons. Such hollow cylinders provide

regions of high and uniform fission-neutron flux of approximately the same total magnitude as the general flux of thermal neutrons in the reactor core. The maximum thermal flux obtainable in BEPO (Harwell) is 2×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$, a figure which is typical of most fair-sized graphite-moderated natural-uranium reactors. Higher fluxes are obtainable in heavy-water-moderated reactors such as the NRX pile at Chalk River. The recently constructed Materials Testing Reactor (Huffman 1954) has the highest fluxes of neutrons so far available, approximately 2×10^{14} neutrons $\text{cm}^{-2} \text{sec}^{-1}$.

Both the energy spectrum and the total integrated flux are needed to specify an irradiation dose. It is usual to choose a fixed position in a reactor and measure doses in terms of integrated thermal flux at that point. Fast neutron dose can then be estimated from theoretical or experimental knowledge of the ratio of fast to thermal flux. Neither the theoretical nor the experimental determinations of these ratios are at all easy or accurate (Barschall *et al.* 1952).

Fast neutrons produce primary knock-ons uniformly throughout large specimens, and the size of the specimens is primarily limited by practical considerations such as the size of experimental holes and the difficulty of handling radioactive materials. Temperature control of irradiations is somewhat troublesome at temperatures other than that of the reactor; controlled temperatures as low as -150°C have been reported (Blewitt and Coltman 1954, McReynolds *et al.* 1954).

The presence of γ -radiation and nuclear transmutations induced by thermal neutrons may produce ionization effects and impurity effects. The first of these cannot be avoided by any method of irradiation so far used; the second can be serious in materials where the transmutation cross section greatly exceeds the scattering cross section. Inside hollow uranium cylinders the high ratio of fast to slow flux reduces transmutation effects considerably; for the worst cases the thermal flux can be further reduced by cadmium shielding (Cook and Cushing 1953).

4.1.2. Thermal neutron reactions.

Thermal neutron reactions may be turned to good use in a few cases where the reactions produce massive particles. The three most useful reactions of this type are:

${}^6\text{Li}(\text{n},\alpha){}^3\text{H} + 4.8 \text{ Mev}$, natural cross section 70 barns.

${}^{10}\text{B}(\text{n},\alpha){}^7\text{Li} + 2.4 \text{ Mev}$, natural cross section 750 barns.

${}^{235}\text{U}(\text{n},\text{f})$ fission fragments -160 Mev , natural cross section 3.92 barns.

The cross sections are for 0.025 ev neutrons, and the energies quoted are the average kinetic energy shared by the massive particles and recoil nuclei. When the fast and thermal neutron fluxes are equal, these reactions all produce displaced atoms at some ten to a hundred times the rate produced by fast neutron collisions, and the rates can be still further increased by using materials containing the reacting isotope in enriched proportions.

Values of the doses accurate to between 1% and 10% are readily obtained from the known cross sections and the integrated thermal neutron flux which can be obtained from the activity of monitoring cobalt foils placed with the specimens. The size of the samples is restricted by the necessity of removing heat liberated in the reactions and also, in the case of boron compounds especially,

by the strong absorption of thermal neutrons in the samples. The destruction of the reacting nuclei, and the accumulation of reaction products give impurity effects, which become large as the integrated thermal neutron fluxes approach the reciprocal of the reaction cross sections.

4.2. Cyclotron Irradiation

Mono-energetic beams of protons, deuterons and α -particles, with energy between 5 and 50 mev and current density of 10^{-6} A cm $^{-2}$ can be extracted fairly readily from small cyclotrons. This current density corresponds to a proton flux of 6.24×10^{12} particles cm $^{-2}$ sec $^{-1}$. Convenient irradiation times are shorter than those of reactor irradiations, but the rate at which damage is introduced is usually considerably higher.

The techniques of cyclotron irradiation have been described in detail by Yockey *et al.* (1954). Doses may be measured to within about 10% by integrating the current flowing to the specimens by the Faraday cup method. To ensure that the bombarding particles are effectively mono-energetic, thin specimens must be used, which are not suitable for the measurement of some physical properties. The energy absorbed by the specimen renders close temperature control difficult. Nuclear transmutations are usually quite negligible.

Cyclotron produced neutrons have been used (Sidhu and Henry 1950, Hamilton, Putnam and Ehrmann 1952), but the fluxes available appear to be much lower than those obtainable in reactors.

4.3. Van de Graaff Irradiation

Van de Graaff machines have been used for electron irradiations. Beam currents of about 6×10^{14} electrons cm $^{-2}$ sec $^{-1}$ are readily available. The cross sections for primary knock-ons are about a thousand times less than those for cyclotron produced particles and Van de Graaff machines generally induce damage some ten to a hundred times slower than cyclotrons. The techniques are very similar to cyclotron irradiation, but since the electron ranges are greater than for heavy charged particles with the same energy, higher beam currents and thicker specimens can be used before insuperable heat transfer problems are encountered. γ -radiation is always present; transmutations are negligible.

The energies of the electrons are in the range 0.5 to 5 mev, and the minimum electron energy required to produce a primary knock-on lies in this range for the majority of elements. The determinations of displacement energy E_d referred to in § 2.1.1 have all been made by measuring the damage as a function of electron energy, and extrapolating to zero damage. Results obtained by Klontz (1952) are shown at figure 4.1.

4.4. Gamma Irradiation

A 100 curie source provides γ -ray fluxes of about 10^{11} quanta cm $^{-2}$ sec $^{-1}$. The cross sections for primary displacements are low and only very small fractions of displaced atoms can be produced in a convenient time. Dugdale (1955) has used γ -radiation from ^{60}Co , which has a mean energy of 1.3 mev.

4.5. Natural Radioactivity

The spontaneous radioactivity of heavy elements produces α -particles of various energies in the range 4–10 mev (Briggs 1954) which have been used to

produce irradiation damage. The fluxes obtainable are largest with the shortest lived elements when they can be concentrated in sufficient bulk. Probably the best available is polonium (half-life 140 days), which was used by Brattain and Pearson (1950). In principle, a flux of about 10^{11} α -particles $\text{cm}^{-2} \text{sec}^{-1}$ is obtainable at the surface of a sufficiently thick source. Brattain and Pearson worked with a flux of 2×10^6 α -particles $\text{cm}^{-2} \text{sec}^{-1}$. Marsden (1910), using radon, worked with up to 10^9 α -particles $\text{cm}^{-2} \text{sec}^{-1}$. The α -particles only penetrate distances of about 10^{-3} cm, which places severe restrictions (with external sources) on the type of experiment that is feasible.

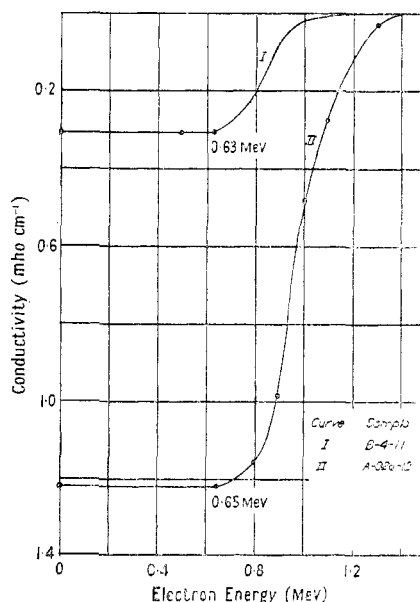


Figure 4.1. Extrapolation curves used in the determination of threshold energy in germanium. The electron irradiations were carried out at 77°K (Klontz 1952).

Very large doses have been produced in large volumes by the natural radioactivity of uranium and thorium contained in minerals, acting for times of between 10^8 and 10^9 years. In 10^9 years 15% of the ^{238}U originally contained in a mineral has decayed to lead in eight separate α -disintegrations, each of which produces about 2000 displaced atoms mainly due to the recoiling heavy nucleus. Consequently the atoms of a mineral 10^9 years old and containing 10% (atomic) of uranium have all been displaced on the average about 250 times. Doses in thorium-containing minerals are somewhat less because the half-life of thorium is longer, and only six α -disintegrations occur in its decay scheme. The range of the recoiling nuclei is very short ($\sim 10^{-6}$ cm, Bohr 1948), and so damage caused by radioactive inclusions is essentially due to the α -particles.

Minerals containing radioactive elements only as impurities exhibit a wide range of doses from one specimen to another, and it is possible to study effects as a function of dose (e.g. Hurley and Fairbairn 1953). Doses in radioactive minerals are measured by essentially the same methods as are used for age determinations, the most usual of which is the chemical estimation of Pb and U. Hurley and Fairbairn used a variety of methods to overcome the difficulties

presented by heterogeneous distribution of radioactivity, and the simultaneous presence of thorium. Their accuracy appears to be within 10% to 20%.

We summarize the main features of the various irradiation techniques with some illustrative figures in table 4.1.

Table 4.1. Summary of Irradiation Techniques

Radiation	Convenient energy (MeV)	Convenient flux (particles $\text{cm}^{-2} \text{sec}^{-1}$)	Convenient time	No. of displacements per atom
Neutrons	2	10^{13}	1 month	10^{-1} in Cu
Slow neutron reaction $^{10}\text{B} (n, \alpha)$	^7Li , 0.87 ^4He , 1.53	10^{13} (neutrons)	1 month	2 in BN.
Deuterons	10	6×10^{12}	10 hours	10^{-2} in Cu
Electrons	2	6×10^{14}	10 hours	10^{-3} in Cu
γ -rays	1.3	10^{11}	1 month	10^{-8} in Cu
Natural sources (External)	5.3(a)	10^3	1 month	5×10^{-4} in Cu [†]
Natural sources (Minerals)	~ 6 (a)	—	10^3 years	100 in ThSiO_4

[†] Average over range of 10^{-8} cm

§ 5. EXPERIMENTAL RESULTS

5.1. Metals

Except for changes in yield stress, the physical properties of metals are not greatly affected by irradiation at room temperature, largely because of the ease with which lattice defects anneal out. In aluminium, for instance, room temperature irradiation causes no observable changes of physical properties, including yield stress, although irradiation (and measurement) at liquid nitrogen temperatures gives marked alterations. Thus a study of irradiation phenomena in metals involves irradiation at the lowest possible temperatures in order to freeze in all the lattice defects. A large proportion of the measurements have been made on electrical resistivity which is, perhaps, the easiest physical property to measure under these conditions.

5.1.1. Copper.

Martin *et al.* (1951) bombarded copper at -150°C with 35 mev α -particles and found an increase in electrical resistivity, the greater part of which annealed out at room temperature. Marx *et al.* (1952) using 12 mev deuterons at -150°C measured resistivity changes as a function of integrated deuteron flux up to about 10^{17} deuterons cm^{-2} . They carried out annealing experiments which showed the recovery to have an activation energy of 0.20 ± 0.05 ev at -110°C and about 1 ev at room temperature. More accurate measurements by Overhauser (1953) using the same irradiation conditions, showed that the activation energy rose from 0.2 ev as annealing proceeded and reached a steady value of 0.68 ev at -30°C , as shown in figure 5.1. When this recovery was complete no other well-defined activation energy was found at annealing temperatures up to 160°C . Eggleston (1953) using 35 mev α -particles, found an activation energy of 0.72 ev between -65 and -20°C and a second well-defined activation energy of 2.12 ev between 250 and 300°C . In a further investigation of the lowest activation energy for recovery, Cooper *et al.* (1954) carried out deuteron irradiations at 12 and 16°K . On heating the copper after irradiation they observed a sharp drop of 50% in the excess resistivity at 40°K indicative of a unique activation energy of about 0.1 ev.

In all of these irradiations the specimens were sufficiently thin to allow complete penetration by the charged particles, and the damage consisted of small groups of interstitials and vacancies.

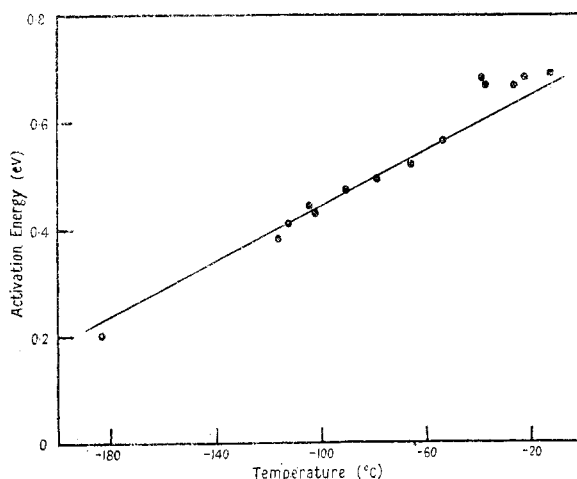


Figure 5.1. Activation energy for recovery in copper. The line extrapolates to zero activation energy at 0°K (Overhauser 1953).

Marx *et al.* (1952) suggested several possible reactions between interstitials and vacancies which could explain their early observations, and Overhauser (1953) ascribed the 0.7 eV reaction to the migration of vacancies. Huntington and Seitz (1942) and Huntington (1942) had previously calculated the migration activation energies for interstitials and vacancies as $\frac{1}{2}$ eV and 1 eV respectively; the more recent calculations of Huntington (1953) give $\frac{1}{4}$ eV for interstitials. Brinkman *et al.* (1954) have discussed in detail the migration of interstitials and vacancies. They associated the activation energy of 1.25 eV, found by Bowen, Eggleston and Kropschot (1952) for the annealing of cold-worked copper, with the migration of vacancies. (This association is supported by the activation energy of 1.2 eV for vacancy migration which can be deduced from electrical measurements of Meehan and Eggleston (1954) and the self-diffusion activation energy.) The lower activation energies found in irradiated copper were therefore associated with interstitial migration.

Because of distortion of the lattice in the neighbourhood of interstitials and vacancies, the activation energy for the annealing of close interstitial vacancy pairs will be appreciably less than that required for the migration of interstitials in the undistorted lattice (Marx *et al.* 1952, Overhauser 1953). Thus it is possible to argue that the marked recovery at 40°K is due to the annealing of interstitials in the positions closest to vacancies and that the activation energy rises as the average interstitial-vacancy separation increases, until 0.7 eV represents the activation energy for migration of interstitials in a lattice with small *average* strain. The kinetics of the 0.7 eV reaction observed by Overhauser and Eggleston differ from those of the expected second-order reaction, and the calculations of Overhauser show that the discrepancy can reasonably be attributed to lattice strain.

The measurements of Overhauser (1954) on the stored energy liberated by deuteron irradiated copper (0.052 cal g⁻¹ for 10¹⁷ deuterons cm⁻²) provide a partial

confirmation for the above interpretation. Between -150°C and room temperature he found that the ratio of stored energy released to resistivity recovered was constant, indicating that a single process (i.e. the return of interstitials to vacancies) was operative. In addition, McDonell and Kierstead (1954) have observed a decrease in the density of copper irradiated at -190°C by 21 mev deuterons. As we shall see, their results (shown in figure 5.2) suggest that interstitials are present at -190°C and that the majority are removed by annealing at room temperature.†

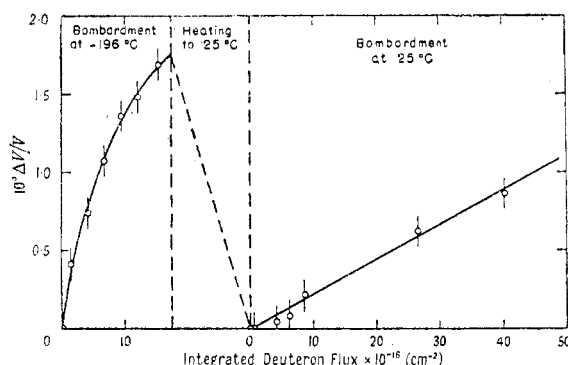


Figure 5.2. Specific volume increase induced by deuteron bombardment (McDonell and Kierstead 1954).

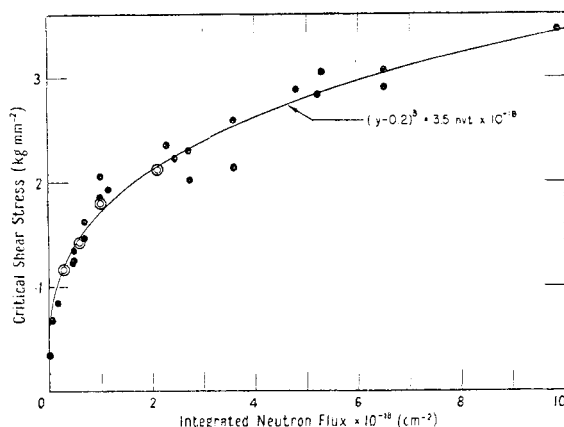


Figure 5.3. Change in yield stress of copper due to neutron irradiation at room temperature (Blewitt, private communication).

The increase in yield stress observed by Blewitt and Coltman (1951) (see figure 5.3) and McReynolds *et al.* (1954), and the increase in hardness observed by Billington and Siegel (1950) and Dixon and Meehan (1953) may be expected for almost any type of lattice defect. Redman *et al.* (1953) found an activation energy for recovery of 2.2 ev which is close both to the 2.12 ev observed by Eggleston (1953) in the resistivity recovery and to the activation energy of 2.02 ± 0.15 ev for self-diffusion (Kubaschewski 1950). Seitz (1952b) suggested that interstitials and vacancies may coagulate into groups which would be removed by a self-diffusion process, and it is possible that such groups may be responsible

† Note added in proof. More recent measurements (Kierstead 1954) suggest that the volume changes may be five times smaller than the changes reported by McDonell and Kierstead (1954).

for the observed phenomena. There is, however, no positive evidence for the nature of the defects which recover with 2.1 eV activation energy.

In addition to the theoretical calculations, already mentioned, of the displacement energy and migration activation energies in copper, attempts have been made to predict the effect of lattice defects on the physical properties. Tucker and Sampson (1954) conclude that 1% of interstitials will give rise to a 1% increase of lattice parameter (3% decrease in density) while 1% of vacancies will give $\frac{1}{3}$ % decrease of lattice parameter. Dexter (1952) calculated an increase in the electrical resistivity of copper, silver and gold of $0.6\mu\Omega$ cm for 1% of interstitials and $0.4\mu\Omega$ cm for 1% of vacancies, while Jongenburger (1953 a, b) calculated 1.3, 1.5 and $1.5\mu\Omega$ cm for 1% of vacancies in copper, silver and gold respectively. Dienes (1952 a) estimated that 1% of vacancies should decrease the elastic moduli by 1% and that 1% of interstitials should increase the moduli by about 10%. While the magnitudes of the effects of interstitials and vacancies may not be so different as this (Nabarro 1952, Dienes 1952 b) it would appear that equal numbers of interstitials and vacancies should increase the elastic moduli. However, Dieckamp and Crittenden (1954) have reported a decrease in the shear modulus of copper irradiated and measured at -175°C , and Bowen and Rodeback (1953), from electrical measurements, found a decrease in the Debye temperature of irradiated copper.

Witzig (1952) observed no change in the creep rate of copper irradiated with 16 MeV deuterons at 260°C ; his calculations showed that little change would be expected either from the thermal spike model or from an increase, based on the collision model, of the equilibrium number of vacancies.

Only in the experiments of Cooper *et al.* (1954) can it be assumed that most of the displaced atoms are retained in interstitial sites. For an average deuteron energy of 10 MeV, we calculate 3.8×10^{-3} displaced atoms per atom for a dose of 10^{17} deuterons cm^{-2} . Assuming a resistance increase of $2\mu\Omega$ cm for 1% of Frenkel defects, the corresponding increase of resistivity should be $0.8\mu\Omega$ cm. The resistivity increase observed by Cooper *et al.* for this dose was $0.19\mu\Omega$ cm; the initial rate of change of resistivity was $0.23\mu\Omega$ cm per 10^{17} deuterons cm^{-2} . The stored energy data of Overhauser cannot be compared directly with calculations, since there must have been substantial annealing at the temperature of his irradiations. However, assuming the energy of a Frenkel defect to be 5 eV, he concludes that the extra resistivity due to 1% of Frenkel defects is $11\mu\Omega$ cm. If this estimate is accepted, the discrepancy between observed and calculated resistivity changes in the experiments of Cooper *et al.* is increased to a factor of 16.

The fraction of displaced atoms in the volume of the specimen considered by McDonell and Kierstead should be about 3×10^{-3} per 10^{17} deuterons cm^{-2} , corresponding to a fractional volume increase of 9×10^{-3} . Taking into account the annealing observed by Cooper *et al.*, this agrees quite well with the observed volume increase (initially 2.5×10^{-3} per 10^{17} deuterons cm^{-2}).[†]

The picture which we have of the recovery is therefore as follows. The first stage is the annealing of close pairs with activation energies rising from 0.1 to 0.7 eV; this is followed by almost free diffusion of randomly distributed interstitials with an activation energy of 0.7 eV. During this second stage some groups of interstitials are formed and some interstitials escape to dislocations or grain boundaries, leaving a small excess of vacancies, the removal of which constitutes

[†] See footnote on previous page.

the third stage. Finally, the groups of interstitials are eliminated by a self-diffusion process, recovery being complete at 400°C. Qualitatively, this picture is in reasonable accord with the observations, but the quantitative agreement is not so satisfactory. We have ignored other possible processes, such as the migration of vacancy pairs (Bartlett and Dienes 1953) and the dissociation of groups of defects, which may be important. Our interpretation is not the only possible one (Broom 1954) and its validity can only be determined by further experimental work.

5.1.2. Copper-gold.

A number of irradiation experiments have been carried out with the copper-gold alloy Cu_3Au . This is a typical order-disorder alloy of which a description is given in the review article by Nix and Shockley (1938). For this alloy the Bragg-Williams definition of the degree of order S is $S = 4(r - \frac{1}{4})/3$ where r is the fraction of gold atoms occupying 'gold sites' i.e. lattice sites which are occupied by gold atoms when the alloy is perfectly ordered. $S = 1$ for perfect order and $S = 0$ for disorder. The equilibrium degree of order is zero above the critical temperature (388°C) and increases to unity as the temperature is lowered to 0°K. At room temperature the times necessary to reach equilibrium are so long that all the ordered alloys have appreciably less than the equilibrium of order. If the alloy is quenched after prolonged heating just below the critical temperature, domains of long-range order are present and ordering can proceed readily at 150°C, but if quenched from above the critical temperature, no such domains exist and ordering takes place very much more slowly.

The experiments of Siegel (1949) showed that the ordered alloy was disordered by fast neutron irradiation, and the disordered alloy was little affected. Similar experiments have been carried out by Martin *et al.* (1951), Adam and Dugdale (1951), Glick *et al.* (1952), Glick and Witzig (1953) and Cook and Cushing (1953). The main feature of these subsequent experiments is that, except in high fluxes of fission neutrons, an initial decrease of resistivity, indicative of ordering, can be observed (see figure 5.4).

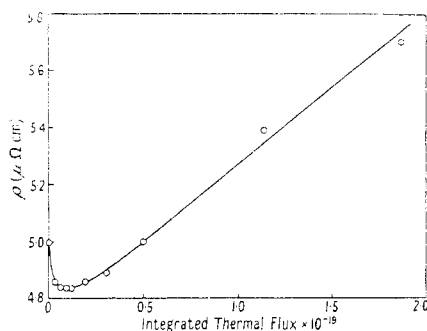


Figure 5.4. Change in resistivity of Cu_3Au due to neutron irradiation (reactor spectrum) at room temperature (Dugdale, private communication).

The experiments of Blewitt and Coltman (1952, 1954) and of Dixon and Bowen (1954) show that the rate of ordering is considerably enhanced *during* irradiation by neutrons and protons, and it is suggested by Blewitt and Coltman that the ordering is due to the diffusion of lattice defects. This suggestion is confirmed by the increased rates of ordering observed *after* short irradiations (producing

little or no disorder) by electrons (Adam, Green and Dugdale 1952, Dixon, Meechan and Brinkman 1953), γ -rays (Dugdale 1955) and neutrons (Coltman and Blewitt 1953). Brinkman *et al.* (1954) argued that it is improbable that the alloy can be ordered by the movement of interstitials, and they postulated that the ordering is due to vacancy migration. Their qualitative arguments are supported by the measurements of Dugdale and Green (1954) who found that the activation energies for ordering were almost the same (0.9 eV) for cold worked, quenched and electron irradiated specimens, since an excess of vacancies would be expected in the first two cases. Brinkman *et al.* (1954) irradiated ordered and disordered specimens with protons at a temperature below -100°C and observed resistivity increases of 4.25 and $0.65\ \mu\Omega\ \text{cm}$ respectively. The specimens were then heated, and between -60 and 0°C both recovered by $0.60\ \mu\Omega\ \text{cm}$. At higher temperatures the resistivity of the ordered specimen decreased by a further $0.45\ \mu\Omega\ \text{cm}$ and that of the disordered specimen decreased by $0.05\ \mu\Omega\ \text{cm}$. They attributed the low temperature recovery to migration of the interstitials, some of which diffuse to dislocations and grain boundaries, and the subsequent recovery of the ordered specimen to migration of the surplus vacancies. The lack of nuclei in the disordered specimen explained the absence of ordering.

The initial decrease of resistivity which occurs during room-temperature neutron irradiation of ordered specimens can be explained in terms of vacancy migration. As discussed in § 2.3, each fast neutron collision will give rise to a highly disordered region. After the migration of interstitials, the surplus vacancies assist further ordering of the surrounding matrix which, although termed ordered, has not the equilibrium degree of order at temperatures below about 200°C . As the number of disordered regions increases, the migration distance of vacancies decreases (Blewitt and Coltman 1954) and this, together with the increasing order of the matrix, leads to a saturation of the order, after which disordering predominates. In high fluxes, the vacancies have no time to move before their ordering efficiency is seriously reduced. Because practically every type of radiation which would be expected to produce displaced atoms has been observed to enhance the rate of ordering of Cu_3Au , the above interpretation seems preferable to the assumption (Cook and Cushing 1953) that mercury, produced by thermal neutron absorption, increases the rate of ordering.

Dugdale (1955) has found that the displacement energy for copper in Cu_3Au is appreciably less than the 25 eV found in pure copper and is probably about 10 eV. He has also observed that the integrated flux of cobalt γ -rays is approximately 200 times the integrated flux of 1 MeV electrons needed to produce the same increase in ordering rate. This is in reasonable agreement with the ratio, calculated by the methods given in § 2, of the integrated fluxes needed to produce a given fraction of displaced atoms. On the basis of this data, ordering can be observed after an irradiation which displaces only 10^{-3} of the atoms.

Siegel (1949) and Cook and Cushing (1953) found that regions of about 10^4 atoms are disordered at each fast neutron collision and Seitz (1949) has calculated (using $E_d=25$ eV) that the number of displaced atoms would be an order of magnitude less. He was therefore led to postulate the existence of high temperature thermal spikes to explain the observed disordering. For this alloy, in which the atomic weights are very different, calculations are difficult, but it would appear that the replacement collisions used (Kinchin and Pease 1955) to explain the disordering of a similar alloy (Ni_3Mn) offer an alternative explanation.

Fillnow *et al.* (1953) have found an increase in hardness in both ordered and disordered Cu_3Au , analogous to the hardness changes observed in copper.

The model which we used to explain irradiation effects in copper seems to be applicable to the case of Cu_3Au , taking into account the smaller values of displacement and activation energies.

5.1.3. Other metals and alloys.

(a) *Electrical properties.* Marx *et al.* (1952) measured resistivity changes in silver, gold, nickel and tantalum irradiated with deuterons at -150°C . The largest effects were observed in tantalum, and the rate of increase of resistivity fell off with irradiation dose in all cases. Larger changes were observed in silver and gold at 12°K by Cooper *et al.* (1954). Their results for copper, silver and gold are summarized in table 5.1, in which changes observed for an integrated flux of 10^{17} deuterons cm^{-2} are compared with those calculated from the initial rate of change of resistivity; even at 12°K there appears to be some annealing.

Table 5.1. Change in Resistivity ($\mu\Omega$ cm) for 10^{17} deuterons cm^{-2} .
Deuteron energy 12 mev

		Copper	Silver	Gold
12°K	Extrapolated from initial slope	0.23	0.26	0.38
	Observed	0.19	0.20	0.31
135°K	Extrapolated from initial slope	0.09	0.14	0.26
	Observed	0.06	0.10	0.19

On raising the temperature after irradiation, the resistivity of silver dropped sharply at about 30°K by 20% of the radiation-induced increase (compared with the 50% drop at 40°K in copper), while for gold no sharp drop was observed. Assuming in all cases 25 ev for the displacement energy and $2\mu\Omega$ cm for the resistivity due to 1% of Frenkel defects, the calculated increases of resistivity for copper, silver and gold are 0.8, 1.1 and $1.6\mu\Omega$ cm respectively. The observed resistivity changes show the same trend as the calculated values, but are appreciably smaller.

Activation energies of about 0.2 ev were observed by Marx *et al.* for silver and gold, as for copper; even for nickel and tantalum, which retained a much larger fraction of the change at room temperature, annealing was observed at -110°C with an activation energy of about 0.3 ev.

Dugdale (1952) has measured changes in the resistivity of platinum due to neutron irradiation and has shown that the activation energy for recovery (1.19 ev) is close to that observed in the recovery of cold worked specimens. The measurements were made only over a small temperature range and it was not shown that the activation energies were 'well-defined' in both cases. There is, however, a strong presumption that both effects were due to vacancy migration.

Randolph (1952) found an increase in the resistivity of molybdenum using 10 mev deuterons, and Kinchin (see Dugdale 1955) has measured the increase of resistivity of molybdenum and tungsten bombarded with fission neutrons at a temperature of about 30°C (figure 5.5). The activation energy for recovery in molybdenum rises from 1.20 to 1.35 ev during annealing at temperatures up to 190°C . The apparent order of reaction (§ 3) then changes and the activation energy reaches a steady value of 1.47 ev between 230 and 300°C , at which

temperature 90% of the change has recovered. Only 20% of the change in tungsten recovers at temperatures up to 300°C and the activation energy rises from 1.2 to over 1.6 eV. Resistivity changes in aluminium irradiated by neutrons at low temperatures (McReynolds *et al.* 1954) anneal out completely between -80 and -20°C.

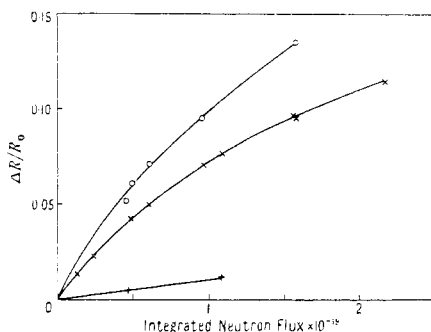


Figure 5.5. Fractional resistance increase of metals irradiated with fission neutrons at 30°C. o tungsten; × molybdenum; + platinum (Kinchin).

Wruck and Wert (1954) irradiated iron, cobalt and nickel with 10 MeV deuterons at -150°C and found that the increase of resistivity in iron is about five times greater than that in cobalt or nickel. Neutron irradiation also gives a larger change in iron and the authors attribute this to the difference in structure.

Aronin (1954) has measured changes of resistivity and of magnetic properties in the order-disorder alloy Ni_3Mn after neutron irradiation. From his results he calculated that each fast neutron collision gave rise to about 5000 random replacements. The picture, used by Cook and Cushing (1953), of islands of disorder in an ordered matrix is more applicable to the case of fast neutron bombardment, and this picture requires about 10^4 random replacements per fast neutron collision. The number calculated by Kinchin and Pease (1955) was 7450, of which 1350 were due to the random return of displaced atoms and 6100 were due to replacement collisions. Eggleston and Bowman (1953) have observed large increases in the resistivity of β -brass irradiated with α -particles at -100°C, with complete recovery below room temperature; the effects were attributed to disordering. Rosenblatt *et al.* (1954) found that the resistivity of α -brass *decreased* during neutron irradiation and that the resistivity recovered its original value after annealing at 170°C. This behaviour is thought to be due to an ordering of the alloy.

Changes in the thermoelectric power of iron and constantan have been reported by Andrew and Davidson (1953).

(b) *Density.* Tucker and Sampson (1954) have reported lattice expansions of the order of $5 \times 10^{-2}\%$ in various neutron irradiated metals and Adam (see Dugdale 1955) has found an increase of $1.5 \times 10^{-2}\%$ in the lattice spacing of molybdenum after an irradiation of 2.3×10^{19} fission neutrons cm^{-2} at 30°C. These small changes suggest that, because of rapid recovery, relatively few interstitials remain after room temperature irradiation.

(c) *Mechanical properties.* Increases in yield stress or hardness have been found in aluminium at low temperatures (McReynolds *et al.* 1954), molybdenum (Geib and Grace 1952), iron, zinc (Kunz and Holden 1954), mild steel (Meyer 1954) and stainless steels (Billington and Siegel 1950). In iron, as in copper,

the activation energy for recovery (3.1 ev) is close to the activation energy for self-diffusion.

(d) *Diffusion and creep.* Johnson and Martin (1952) looked for a change in the self-diffusion coefficient of silver under proton bombardment, and found no appreciable change at the lowest temperature of measurement (555°C). Their calculations showed that the equilibrium concentration of vacancies produced by the radiation would be expected to be small compared with the vacancy concentration in thermal equilibrium.

These results may not appear at first sight to be consistent with the explanation of, for instance, the enhanced ordering rates in Cu_3Au , where the concentration of vacancies due to radiation is supposed to exceed the equilibrium concentration. This is because the diffusion lengths needed to measure bulk diffusion coefficients experimentally are so great that this type of experiment cannot be carried out in a temperature range where radiation effects produce a significant increase in the equilibrium number of vacancies or interstitials.

The experiments of Andrade (1945) on the effect of α -particle bombardment on the creep rate of cadmium have been repeated by Makin (1955) who found no significant change in creep rate. Jones, Munro and Hancock (1954) found no change in the creep rate of aluminium due to neutron irradiation.

(e) *Phase transformations and precipitation.* Fleeman (1953, 1954) has found that the transformation from white to grey tin is nucleated by neutron irradiation, and Denney (1953, 1954 a) showed that iron precipitated in copper is transformed from the face-centred cubic to the stable ferromagnetic body-centred cubic structure under the influence of electron irradiation. The threshold found by Denney (0.5 mev) gives a lower limit of 25 ev to the displacement energy for face-centred cubic iron. The transformation could be induced by vacancies formed in the copper matrix, for which the threshold energy is known to be 0.49 mev, or by the displacement of iron atoms. Denney (1954 b) subsequently found that proton irradiation causes the ferromagnetism of the transformed precipitate to *decrease* and interpreted this experiment in terms of thermal spikes. Solution of the precipitate by replacement collisions may, however, be the explanation.

Billington and Siegel (1950) studied the effects of fast neutron irradiation on supersaturated solutions of beryllium in copper. More extensive measurements by Murray and Taylor (1954) showed that the changes in resistivity and hardness are very similar to those produced by ageing at temperatures of about 100°C and they are thought to be due to the formation of precipitate nuclei. The similarity was checked by retrogression experiments (solution of the nuclei) at higher temperatures. Latent changes, which become apparent on subsequent heating, are introduced by irradiation at low temperatures (Cleland, Billington and Crawford 1953). These experiments suggest that the precipitation is nucleated by the migration of lattice defects (probably vacancies). Density changes observed by Murray and Taylor were not explained.

5.2. Semiconductors

5.2.1. Germanium.

Since a typical sample of n-type germanium may contain only 10^{-7} free electrons per atom and each displaced atom removes of the order of one free electron, it is evident that the electrical properties of semiconductors are extremely sensitive to radiation.

The changes of conductivity of n-type (electron excess) and p-type (electron deficit or hole excess) germanium due to deuteron irradiation are shown in figure 5.6 (Fan and Lark-Horovitz 1955). It will be seen that the conductivity alters by several orders of magnitude, in contrast with the relatively small changes in metals. Changes of conductivity and Hall coefficient have been extensively

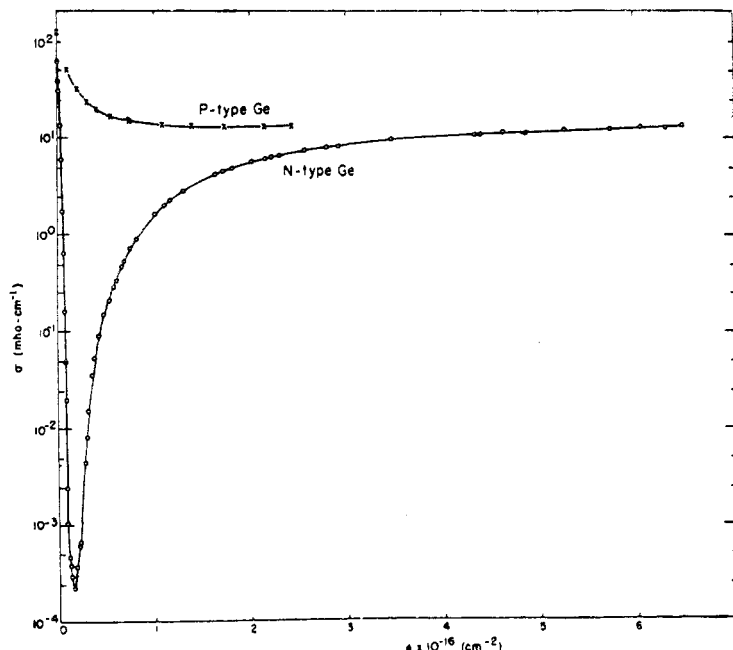


Figure 5.6. Change in conductivity of deuteron-irradiated germanium as a function of dose (Fan and Lark-Horovitz 1955).

studied using irradiation with heavy charged particles (Lark-Horovitz, Bleuler, Davis and Tendam 1948, Brattain and Pearson 1950, Forster, Fan and Lark-Horovitz 1952) and neutrons (Davis, Johnson, Lark-Horovitz and Siegel 1948, Johnson and Lark-Horovitz 1949, Crawford and Lark-Horovitz 1950, Lark-Horovitz 1951, Cleland *et al.* 1951 a, b). The effects of nuclear transmutations during neutron irradiation have been shown to be small, in agreement with calculations based on the known cross sections (Cleland, Lark-Horovitz and Pigg 1950). Measurements of Hall coefficient demonstrate that n-type germanium is converted to p-type by irradiation, and confirm that the irradiation effects are due largely to change in the numbers of charge carriers and not to any changes in mean free path. Stevens, Cleland and Crawford (1954) have measured changes in diamagnetic susceptibility corresponding to the changes in electron concentration.

James and Lark-Horovitz (1951) have given an explanation of the effects of neutron irradiation. They consider that vacancies act as electron traps (sometimes called acceptors) and conclude that each vacancy produces two localized empty levels in the forbidden band as shown in figure 5.7. Similarly interstitials act as donors of electrons (sometimes called hole traps) and each interstitial produces two localized filled levels, also shown in figure 5.7. Each interstitial-vacancy pair therefore produces four localized levels and two electrons. If n-type germanium, with an excess of electrons in the conduction band, is irradiated, the lower empty

levels become filled, and each interstitial-vacancy pair removes two electrons. If the material initially has a large excess of electrons, the conductivity is almost proportional to the number of electrons and the conductivity therefore decreases linearly. As the conduction band is emptied, with a corresponding depression of the Fermi level, the higher donor level ceases to be fully occupied, and at the point of minimum conductivity, when the Fermi level is near the middle of the forbidden band, only one electron is trapped per interstitial-vacancy pair. This agrees with the observation that the minimum conductivity occurs at approximately twice the dose which would be expected from a linear extrapolation of the early part of the conductivity-dose curve.

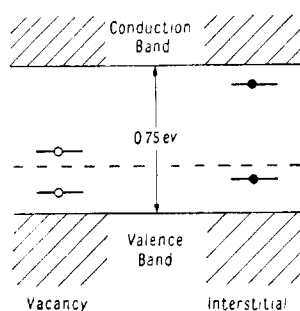


Figure 5.7. Energy levels in irradiated germanium (after James and Lark-Horovitz 1951).

On irradiation of high conductivity p-type germanium, with a large excess of positive holes in the conduction band, electrons from the interstitials drop into the conduction band and reduce the number of charge carriers, initially at the rate of two positive holes per interstitial-vacancy pair (see figure 5.6).

After long irradiations, when the number of defects greatly exceeds the initial electron excess or deficit, it would be expected that the Fermi level would reach a limiting position, independent of the nature of the starting material, approximately midway between the second and third highest levels above the valence band shown in figure 5.7. Experiments with neutron irradiation (Cleland *et al.* 1951 b) have shown that the limiting position of the Fermi level is between 0.1 and 0.17 eV above the top of the valence band.

This explanation can be only a qualitative account of the behaviour of germanium irradiated by neutrons or heavy charged particles, since more recent experiments (Forster, Fan and Lark-Horovitz 1953, Crawford *et al.* 1953) have shown that annealing after irradiation at temperatures below -140°C is accompanied by a redistribution of the localized energy levels, which has been tentatively ascribed to the formation of clusters of defects. The energy levels observed after room temperature irradiation cannot therefore be associated with single interstitials and vacancies.

In the case of irradiation by electrons of moderate energy, when isolated interstitial-vacancy pairs are produced, Fan and Lark-Horovitz (1955) have shown that there is no alteration of the energy levels on annealing and only the number of trapping centres is changed. They have found three localized energy levels in electron irradiated germanium.

The displacement energy for germanium (31 eV) has been determined by Klontz and Lark-Horovitz (1951, 1952). Klontz (1952) also found $dn_e/d\phi$, the number of electrons trapped per cm^3 per unit integrated electron flux. His

results, together with those of Brown, Fletcher and Wright (1953) and Cleland *et al.* (1951 a) are compared in table 5.2 with the numbers of displaced atoms per cm³ per unit integrated flux $dN/d\phi$ calculated by the methods given in § 2.

Table 5.2. Observed and Calculated Damage Rates in Germanium

Author	Radiation	Temperature	$dn_e/d\phi$	$dN/d\phi$
Klontz	1.5 Mev electrons	77°K	1.1	1.2
Klontz	1.5 Mev electrons	Room	0.6	1.2
Brown <i>et al.</i>	3 Mev electrons	Room	1.4	2.6
Cleland <i>et al.</i>	Pile neutrons	Room	3.2	7

Assuming that two electrons are trapped by each interstitial-vacancy pair, the observed and calculated numbers of trapped electrons in the low-temperature experiment of Klontz agree to within a factor of 2. The greater discrepancies for room temperature bombardments are probably due to the annealing which is known to occur below room temperature.

In the initial stages of bombardment of n-type germanium with 5.3 Mev α -particles, Brattain and Pearson (1950) found 78 electrons trapped per incident α -particle at room temperature. Calculations by the methods of § 2 give 85 displaced atoms per α -particle.

Brown *et al.* (1953) studied the annealing of electron irradiated germanium and found two annealing stages above room temperature, which they interpreted in terms of the theories (§ 3) developed by Fletcher and Brown (1953), assuming vacancies to be more mobile than interstitials. The measurements of Mayburg (1954) seem to show that interstitials are the more mobile. Brown *et al.* concluded that the first stage, with an activation energy of 1.58 eV, was due to the monomolecular recombination of very close pairs, and that the second stage, with an activation energy of 1.78 eV, was a 'liberation' process of the kind described in § 3.1.1.

Florida, Holt and Stephen (1954) have found that neutron irradiation causes a decrease in the hole life-time in germanium and suggest that the lattice defects are recombination centres.

5.2.2. Silicon.

The effects of irradiation on silicon are in general similar to those on germanium. The limiting position of the Fermi level appears to be close to the middle of the forbidden band, so that both n-type and p-type silicon finish, after long neutron irradiation, with very high resistivity. The trapping levels appear to lie at about 0.7 to 0.8 eV below the conduction band, and this is confirmed by the observation of a strong infra-red absorption band at 0.7 eV (Johnson and Lark-Horovitz 1949, Lark-Horovitz, Becker, Davis and Fan 1950, Forster, Fan and Lark-Horovitz 1952).

Measurements of the specific heat of neutron-irradiated silicon by Keesom, Lark-Horovitz and Pearlman (1952) show that the linear electronic contribution vanishes in accordance with the electrical measurements, while the Debye temperature decreases. This suggests a decrease of elastic moduli which measurements by Binnie and Liebschutz (1954) seem to confirm.

5.2.3. Indium antimonide.

Indium antimonide has a narrow (~ 0.2 eV) energy gap between valence

and conduction bands and a high electron mobility. Irradiation by neutrons (Cleland and Crawford 1954 a, b, c) and electrons (Pepper *et al.* 1954) reduces the mobility and changes the number of charge carriers. The distribution of localized energy levels is such that the end product of long irradiation is high resistivity p-type material. The interpretation of the results is more complex than for germanium, since indium antimonide contains two types of atom.

5.2.4. Graphite.

Graphite probably has a slightly overlapping band structure (Kinchin 1953) and is intermediate in properties between metals and semiconductors. The changes in Hall coefficient due to neutron irradiation at 30°C are shown in figure 5.8 and can be explained in terms of trapping of electrons by lattice defects. In

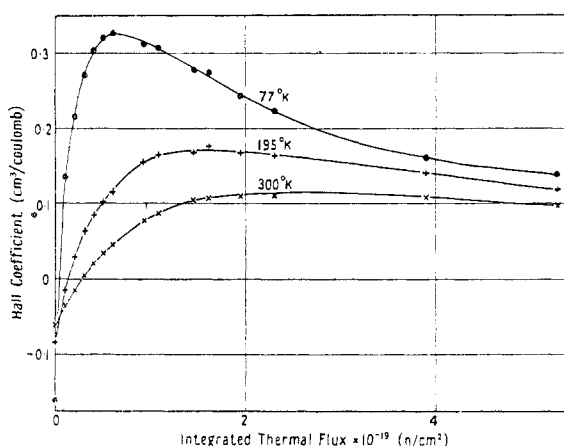


Figure 5.8. Hall coefficient of graphite irradiated with neutrons (reactor spectrum) at 30°C.
 ● measured at 77°K; + measured at 195°K; × measured at 300°K (Kinchin 1954).

this case the changes in mean free path are appreciable, and the combination of decreasing mean free path and increasing carrier (positive hole) concentration leads to a saturation of the resistivity change (Kinchin 1954). The Hall coefficient changes lead to an estimate of 1 trapped electron cm^{-3} per neutron cm^{-2} . The experimental results suggest that the localized energy levels are not fully occupied, and there is considerable uncertainty in estimating the number of displaced atoms from the number of trapped electrons. The calculated (§ 2) number of displaced atoms is also very rough, since it is virtually proportional to L_C , but is within an order of magnitude of the experimental estimate.

5.3. Covalent Compounds

5.3.1. Quartz.

Coloration, embrittlement and fracture of quartz and glasses due to bombardment from naturally radioactive sources were observed many times by early workers (Rutherford, Chadwick and Ellis 1930, Lind and Bardwell 1923 a). Many studies have since been made of the coloration effects (e.g. Choong 1945). It is necessary here, as with all insulators, to distinguish clearly between ionization effects and effects due to displaced atoms. Pile irradiation produces relatively rapid changes in the optical absorption coefficients (Mitchell and Paige 1954), paramagnetic

resonance absorption (Griffiths, Owen and Ward 1954, 1955) and elastic constants (Johnson and Pease 1954) which either cease or continue much more slowly after a short dose. Very similar effects are observed by irradiation with x-rays, and in this case the coloration shows a well-marked saturation (Forman 1949). Johnson and Pease find the ionization doses to half-saturation to be of the order of 0.05 ev per molecule in both cases. It is a characteristic of these ionization effects that they vary widely from one specimen to another, and often from one part to another of the same specimen, and they are attributed to the trapping of electrons at defects already present in the crystal. Direct experiment (Brown and Thomas 1952) strongly suggests that, as supposed by early workers, these defects are impurities; this view is disputed by Dainton and Rowbottom (1954) who suggest that they may be dislocations or vacancies. The defects are hardly likely to be vacancies or interstitials, since fast neutron bombardment bleaches the ionization-induced colour (Johnson and Pease 1954, Mitchell and Paige 1954). In very carefully grown and purified crystals, Brown and Thomas find no ionization colouring.

The first detailed studies of displaced atoms in α -quartz were made by using fast neutron bombardment at about 50°C and low-temperature thermal conductivity measurements (Berman, Klemens, Simon and Fry 1950, Berman 1951, Klemens 1951). The low temperature conductivity is governed by three types of phonon scattering: phonon-phonon scattering which predominates at temperatures above 10°K, scattering from defects of atomic dimensions which is most effective at about 10°K, and boundary scattering which predominates below 10°K. Large decreases of conductivity which were greatest in the region of 10°K (see figure 5.9) were found upon neutron irradiation. For a dose of 1 unit (which we estimate was 10^{18} fast neutrons per cm² with energies between 100 ev and 2 mev in a spectrum given by equation (4.1)) the increased phonon scattering was attributed to about 10^{-4} single defects per atom. The increases in phonon scattering observed at lower temperatures were attributed to increases of boundary scattering due to the presence of relatively large defects. On the implied assumption that these defects contain about 100 atoms, Klemens deduced that their concentration was about 10^{-7} per atom.

At the highest dose used, which corresponds to about 2×10^{19} neutrons cm⁻², the curve of thermal conductivity against temperature is much more similar to that of fused quartz than to that of α -quartz, and the concentration of defects is sufficiently high to produce a state which Klemens referred to as a 'dilute glass'.

The effects of heat treatment of the irradiated quartz were also studied, two main results being obtained. First the stability of the defects is considerable: heating at 100°C for three weeks produced no observable recovery, and heating well above the α - β transition point (573°C) was required before a major proportion of the conductivity change was recovered. Secondly, the large defects annealed more rapidly than the single interstitials and vacancies, although as Berman points out, the same effects might arise by the splitting up of the large defects during heat treatment.

X-ray examination of the effects of neutron bombardment on various forms of quartz provides a second main body of data. Wittels (1953) and Wittels and Sherrill (1954), whose results are confirmed qualitatively by Primak, Fuchs and Day (1953), show there is a transition to an optically isotropic glassy state at doses of about 10^{20} neutrons cm⁻². Beyond this dose, no single-crystal x-ray pattern

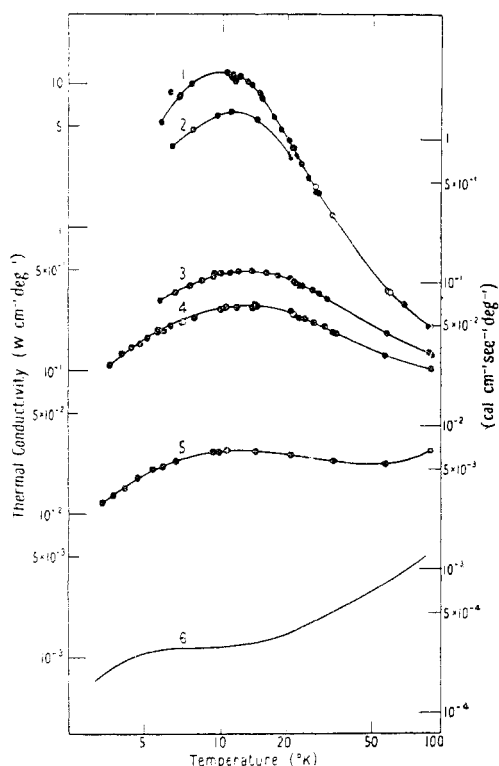


Figure 5.9. Thermal conductivity of neutron irradiated quartz crystal perpendicular to the axis. Cumulative irradiation dose: 1, unirradiated; 2, 0.03 units; 3, 1 unit; 4, 2.4 units; 5, 19 units. Curve 6 shows the thermal conductivity of quartz glass (Berman 1953).

was observed. At lower doses, where the x-ray reflections are still sufficiently sharp, Wittels observed an anisotropic expansion of the structure of α -quartz, the expansion along the a -axis being three times (Johnson and Pease 1954) greater than that along the c -axis. As Wittels points out, the largest interstitial sites available are irregular channels parallel to the c -axis, and the anisotropic expansion is qualitatively well explained by the supposition that atoms are displaced to such sites. Density changes of α -quartz as a function of dose are shown in figure 5.10.

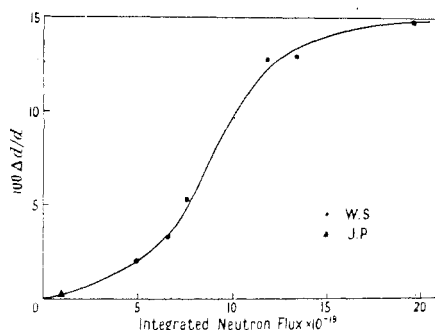


Figure 5.10. Fractional density decrease of neutron-irradiated α -quartz (room temperature). W.S., hydrostatic measurements of Wittels and Sherrill (1954); J.P., x-ray measurement of Johnson and Pease (1954).

A remarkable feature of the curve is the pronounced upward trend of the slope at doses of about 7×10^{19} neutrons cm^{-2} , which cannot be accounted for by any of the simple saturation theories, and is undoubtedly associated with the breakdown of the crystal structure. All four room temperature forms of quartz have the same glassy end-product of prolonged bombardment, and heat treatment (16 hours at 930°C) results in the formation of polycrystalline α -quartz in each case.

McClelland and Donoghue (1953) report decreases in diamagnetic susceptibility. Assuming only a single type of defect to which spin $\frac{1}{2}$ is assigned, they find defect concentrations of 0.78×10^{-3} and 1.1×10^{-3} per atom for doses of 0.51×10^{19} and 3.8×10^{19} neutrons cm^{-2} respectively. These changes are non-linear in the opposite direction to the density changes for doses smaller than 10^{20} neutrons cm^{-2} . That the changes observed are due to paramagnetic defects is shown directly by the reports (Griffiths, Owen and Ward 1954, 1955) of paramagnetic resonance absorption in neutron-irradiated quartz.

The frequency of BT-cut quartz crystal oscillators decreases linearly with neutron irradiation (Johnson and Pease 1954) up to a dose of 10^{19} neutron cm^{-2} , due to a decrease in the elastic constants. At doses much in excess of this the crystals cease to oscillate.

To intercompare these results, it is first necessary to ensure that the dose scales are approximately equivalent. Fortunately, the thermal conductivity studies were based on Harwell (BEPO) irradiations, as were those of Johnson and Pease; these latter find an x-ray density which fits well on the density-dose curve of Wittels and Sherrill. At such a dose, there should be little discrepancy between hydrostatic and x-ray density measurements. Consequently, these three studies are based on approximately the same dose scale which we use in the rest of this section. About 150 atoms will be displaced by each fast neutron collision on this dose scale. McClelland and Donoghue use doses of neutrons with energy greater than 0.5 mev, and their doses may well be effectively five times greater. This would account for the discrepant non-linearity referred to above.

No detailed theory exists which provides a quantitative account of the nature of the irradiation damage, nor is there available an experimental value of E_d . However, the general picture is fairly clear. At very low doses (in the centre of BEPO, $\leq 10^{16}$ neutrons cm^{-2}) ionization effects predominate. From this dose to about 2×10^{19} neutrons cm^{-2} there is a steady accumulation of damage, apparently roughly linear with dose, which probably consists of isolated interstitials and vacancies, together with clusters of defects, the former greatly predominating in number and affecting a greater proportion of the atoms. X-ray powder photographs at 10^{19} neutrons cm^{-2} show no appreciable line broadening, and it may be inferred that long-range order is virtually unaffected. At a dose of 10^{19} neutrons cm^{-2} , the fractional density decrease is 2.3×10^{-3} , the proportion of isolated defects from the conductivity measurements is about 1×10^{-3} , and the calculated proportion of displaced atoms is 4×10^{-3} . This is quite a satisfactory agreement, since the grouping of interstitials and vacancies is likely to produce appreciable instantaneous recovery. At a dose of about 10^{22} neutrons cm^{-2} , 4% of the atoms have been displaced, and from the discussion in § 3.4 one would expect the concentration of interstitials to saturate at about this dose. Instead, however, the long range order breaks down (without producing any macroscopic shattering). From the non-linear upward trend of the density

curve, it appears as if the structure becomes unstable to further accumulation of interstitial atoms, and the damage in this region is a form of phase change to the metamict state. We discuss this change to the metamict state in a later section. The position has been further complicated in the case of quartz by Hurley and Fairbairn's (1953) report that quartz is not found metamict naturally, even when in the presence of radioactivity sufficient to turn other minerals metamict.

5.3.2. Thermal, optical and magnetic properties.

In spite of the success achieved by low-temperature thermal conductivity studies of irradiated quartz, results on other materials are limited to the recently reported results of Berman, Foster and Rosenberg (1955) with neutron-irradiated sapphire (see figure 5.11) and diamond which suggest similar effects to those

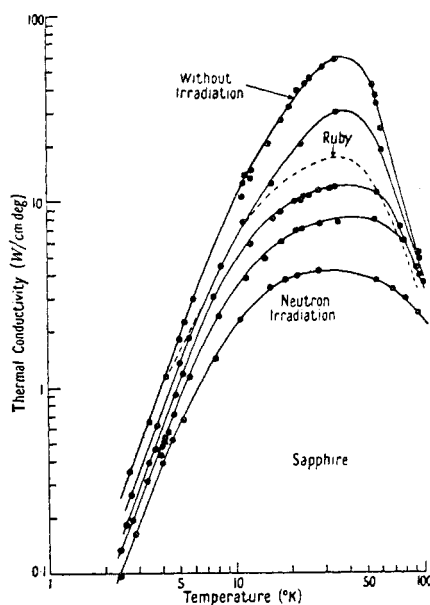


Figure 5.11. Thermal conductivity of sapphire as a function of temperature. Upper curve is for unirradiated sapphire. Lower curves for sapphire irradiated with reactor spectrum neutrons at room temperature for integrated thermal fluxes of 0.15 , 0.9 , 2 and 5×10^{18} neutrons cm^{-2} , from top to bottom (Berman, Foster and Rosenberg 1955).

found in quartz. Stored energies of 100 cal g^{-1} in SiC and diamond, and changes in the specific heat of quartz are referred to by Primak (1954).

Large numbers of observations have been made on coloration, luminescence and phosphorescence of irradiated minerals and glasses. In many cases the changes observed are predominantly ionization effects. We shall deal with coloration effects only in diamond, where a number of carefully controlled experiments have been reported, and where the role of ionization effects is certainly small in most cases.

(a) *Coloration in diamond.* It was shown by Lind and Bardwell (1923 b) that, in contrast to almost all other materials, most diamonds could not be coloured within a reasonable period by β - and γ -rays from natural sources, but that α -

particle bombardment coloured them green. Prolonged heating at 500°C removed the colour. Later work (Cork 1952 a, b, Hardy 1949, Ehrmann 1950 a, b, Hamilton, Putnam and Ehrmann 1952) established that the green coloration extended only for the range of the bombarding ions. The brown colour occasionally induced is certainly a matter of experimental conditions, and is probably due to a combination of heating and bombardment. It appears that the green colour becomes perceptible when about 10^{-5} of the atoms have been displaced.

Dugdale (1953) used pile irradiation and fast electrons to produce the green coloration, but he also found that with sufficiently low energy electrons (0.5 mev) when the majority of the defects must have been isolated Frenkel defects, the colour was always blue. This difference was attributed to the effects of the grouping of the defects produced by the higher energy primary knock-ons. Spectroscopic examination of the absorption and fluorescent spectra of irradiated diamond after heat treatment showed that there are very marked similarities to the spectra of some naturally occurring green diamonds. Prolonged heating of the diamonds even at 1000°C did not bleach the colour completely, but turned the diamonds various shades of brown. Pringsheim and Voreck (1952) and Pringsheim (1953) showed that the major increase in the optical absorption coefficient occurs in the near ultra-violet. Heat treatment produces complex effects which have not so far been interpreted satisfactorily. Further spectrophotometric studies have been reported by Ditchburn *et al.* (1955). The diamonds turned blue by low energy electron bombardment do not have the same spectrum as naturally occurring blue diamonds; moreover, heat treatment of the latter produces no change, while the irradiated diamonds turn yellow-green.

(b) *Magnetic studies.* Paramagnetic resonance studies of neutron and electron irradiated diamonds (Griffiths *et al.* 1954, 1955) have identified two types of defect. The main effect is an isotropic absorption line whose intensity decreases with heat treatment very much as the coloration does. In addition, an anisotropic spectrum is observed, which is much weaker, but whose intensity is not altered by heating at 1000°C . O'Brien and Pryce (1955) ascribe the isotropic band to isolated Frenkel defects, and the anisotropic absorption spectra to interstitial atoms or vacancies, linked together in pairs, with the axis of the pair parallel to one or other of the [110] directions. For a dose of 10^{19} neutrons cm^{-2} the proportion of displaced atoms was estimated from the intensity of the absorption to be 10^{-3} . This is in adequate agreement with the proportion to be expected from the results of § 2.

In addition to their measurements on quartz, McClelland and Donoghue (1953) observed decreases in the diamagnetic susceptibility of MgO , and none in spinel and BeO ; their results on Al_2O_3 were conflicting, and suggest that ionization effects may have contributed to the changes observed.

(c) *Luminescence and photoconductivity.* A considerable body of information is available on the effects of radiation on luminescence in scintillators. Marsden (1910) studied decreases of the luminescence of ZnS , ZnSiO_4 and $\text{BaPt}(\text{CN})_4$, as a function of α -particle bombardment; the luminescence in ZnS was found to be virtually destroyed by doses of about 2×10^{14} α -particles cm^{-2} . Rutherford (1910) interpreted the results in terms of tubes of damage around the track of the α -particles, and obtained tube diameters of 13 Å, 25 Å and 1600 Å in ZnS , ZnSiO_4 and $\text{BaPt}(\text{CN})_4$ respectively. He assumed that the active centres were destroyed. Recently, Smith and Turkevitch (1954) have reported on the effects

of neutron bombardment on the luminescent efficiency of copper-activated ZnS for doses of up to 10^{17} neutrons cm^{-2} . They conclude that the neutron bombardment produces defects which have a large cross section for trapping excited electrons which then return to their normal levels in non-radiative transitions. A somewhat similar effect, a decrease in the efficiency of α -counting in diamond with neutron bombardment, has been reported recently by Benny and Champion (1954).

Day (1953) studied the photoconductivity induced in magnesium oxide by neutron bombardment, and separated the ionization induced effects from the effects of displaced atoms. The latter showed a saturation, interpreted as 2×10^{-9} defects per atom, setting in at about 10^{15} neutrons cm^{-2} . Such a concentration is too low to account for the 0.1% lattice expansion observed by Primak *et al.* (1953) (see § 5.3.3); moreover, the diamagnetic susceptibility changes of McClelland and Donoghue were still increasing at very much higher doses. It thus seems likely that the saturation arises from the mechanism of photoconductivity rather than from a saturation of the number of interstitial atoms.

5.3.3. X-ray studies.

There are available x-ray studies of the effects of room temperature irradiation as a function of dose in zircon (ZrSiO_4) (Hurley and Fairbairn 1952, 1953), boron carbide (Tucker and Senio 1954), various boron compounds (Pease 1954), and reports of pile irradiation effects in black phosphorus (Chipman, Warren and Dienes 1953), and various insulators (Primak, Fuchs and Day 1953, Primak 1954). Most of these are concerned with lattice parameter changes and line broadening. Tucker and Senio have examined diffuse scattering, which they find is of the type predicted for solid solutions by Huang (1947) and others; Binnie and Liebschutz (1954) have also examined diffuse scattering, and small angle scattering has been examined in irradiated diamond (Hayes and Smoluchowski 1953, Robinson, Li and Smoluchowski 1954). The accounts so far published of these studies on diffuse and small angle scattering are too sketchy to warrant detailed discussion herein.

(a) Lattice expansions.

Primak *et al.* report that for a fast neutron dose of about 5×10^{20} neutrons per cm^2 , there are no detectable changes in the x-ray photographs of beryl, GeO_2 , Ge, Si, corundum (Al_2O_3) and rutile (TiO_2); there are lattice expansions of about 0.1% in MgO , spinel (MgO , Al_2O_3) and CaF_2 , and of 1% in diamond and silicon carbide. They also report lattice expansion in Be_2SiO_4 and BeO , Al_2O_3 at a lower dose. Chipman, Warren and Dienes (1953) report a lattice expansion of 0.03% in black phosphorus. They also report the appearance of additional x-ray reflections which seem to be associated with a phase change to the more stable polymorph, red phosphorus. A similar radiation-induced phase change, from white to red phosphorus, is reported by Becquerel (1901). Results obtained by Pease (1954) with powder samples of the compounds BN, B_4C , SrB_6 , ZrB_2 and TiB_2 irradiated by means of the ^{10}B (n, α) reaction show lattice parameter changes of the order of 1% at doses of about 10^{18} thermal neutrons cm^{-2} .

It is thus clear that a characteristic effect of the displacement of atoms is an expansion of the lattice, although this may be too small to detect in some cases. For most of the cases reported by Primak *et al.*, one would expect from the results

of § 2 at least 10% of the atoms to have been displaced, and since the lattice expansions could hardly accommodate more than 1% of interstitials, the proportion of interstitials must be at least a factor of ten down on the proportion of atoms displaced. In the case of the compounds showing no detectable effects, recovery must limit the concentration of interstitials even more drastically.

In non-cubic crystals, the lattice expansion is often significantly anisotropic, which can usually be explained, as in quartz, by the nature of the interstitial site available for the displaced atoms. Thus the layer compounds BN and black phosphorus show big lattice expansions perpendicular to the layers. The small contraction in the plane of the layers of BN can be explained as a consequence of puckering of the layers and of the presence of vacancies. The large contraction along the *c*-axis of B₄C observed by several workers is likewise probably due to a peculiarity of the interstitial sites; it is accompanied by an expansion along the *a*-axis and a net decrease of density.

Rates of variation of the lattice parameters with dose at zero dose, are given in table 5.3. The doses are expressed as the number of bombarding particles per atom (BPPA). In the case of quartz, the bombarding particles are recoil atoms from fast neutron collisions; in the other cases they are α -particles and recoil nuclei produced by the α -disintegrations.

We also show in table 5.3 whether or not line broadening occurs. Line broadening was detected by Primak *et al.* only in quartz and its polymorphs. In this case, we have seen that the line broadening can be associated with transformation to the metamict state. It seems likely that in the case of BN, and also perhaps of black phosphorus, at low doses, the line broadening can be attributed to the direct effects of interstitial atoms on the lattice periodicity.

Table 5.3. Summary of some X-Ray Studies

Substance	Structure	Initial Expansions		Dose to half Saturation (BPPA)	Line Broadening
		$\frac{1}{a} \frac{da}{dx}$	$\frac{1}{c} \frac{dc}{dx}$		
BN	Hex. ^a	-1.1	+8	6×10^{-4}	Assoc. with <i>c</i> axis
B ₄ C	Hex. ^b	+3.5	-5	13×10^{-4}	Some
SrB ₆	Cubic	+5.3	-	3×10^{-4}	None
TiB ₂	Hex. ^{bc}	+13	+6	4×10^{-4}	Slight <i>a</i> axis
ZrB ₂	Hex. ^{bc}	+20	+9	4×10^{-4}	Heavy
ZrSiO ₄	Tetr. ^b	+30 ^e		3×10^{-4}	Heavy
α -quartz	Hex. ^b	+25	+8	Metamict > 3×10^{-4}	Heavy

Notes: ^a Layer structure; ^b three dimensional network; ^c isomorphous; ^d the unit of dose, *x*, is the number of bombarding particles per atom; ^e measured from the (112) reflection only.

(b) *Saturation.* In the boron compounds studied by Pease, the lattice expansions were observed to show a marked saturation phenomenon (an example of this has been shown at figure 3.2), which was attributed to a saturation of the number of interstitial atoms. The case of BN was studied in some detail with the aid of saturation theory. The number *Q* of lattice sites directly adjacent to an interstitial site is twelve, and with this value, saturation is expected to set in at a dose of about 10^{-3} BPPA, with a saturation interstitial concentration of 5%. While saturation was observed to occur at about the right dose, x-ray intensity measurements precluded the expected 5% concentration of interstitials; moreover, irradiation at low temperatures produced much larger effects than at room

temperature. It was therefore concluded that the value of Q was between 100 and 300 at room temperature, and the average number of atoms effectively displaced by a single bombarding particle was only about five. The difference between this last figure and a value of about 50 obtained from Seitz's (1949) expressions was ascribed to virtually instantaneous recovery due to the grouping of the interstitials and vacancies at the end of the ion tracks.

Hurley and Fairbairn (1953) measured the Bragg angle of the 112 reflection from powdered zircons as a function of dose from uranium and thorium impurities, and also obtained a saturation. They fitted an exponential curve to their results and obtained a dose to half-saturation of 3×10^{15} α -particles per milligramme. Primak *et al.* report results for only one dose, so that their results provide no evidence of the presence of saturation.

The doses to half-saturation are given in table 5.3 and, as will be seen, these are all of the same order of magnitude on a scale of bombarding particles per atom. In terms of equation (3.7), this may arise as follows. When Q is large, the number p of displaced atoms per bombarding particle which survive instantaneous recovery is small, because of the grouping of interstitials and vacancies. Likewise when Q is small, p is large. Consequently the saturation dose, $\sim (pQ)^{-1}$, is relatively insensitive to variations of Q from one substance to another. In the case of the zircon results, many more atoms are displaced per bombarding particle, owing to the large contribution from the recoiling nucleus in the α -disintegrations. Because of the great concentration of displaced atoms to be expected in this case, it is possible, however, that very few survive instantaneous recovery.

(c) *Non-saturating effects.* In the case of the boron compounds additional effects of some sort or other were observed for doses exceeding the saturation dose; as an example we show in figure 5.12 line breadths measured on x-ray

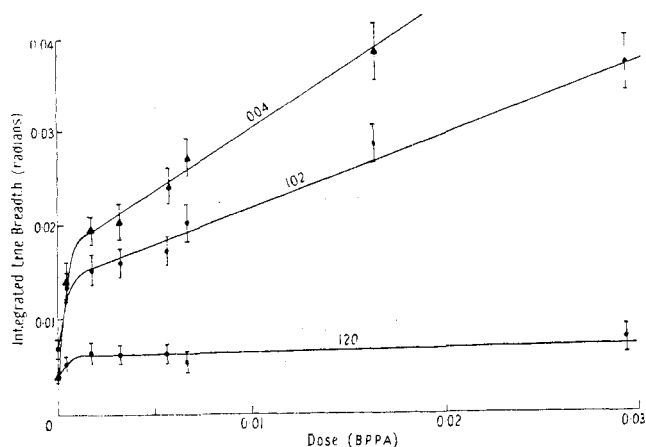


Figure 5.12. Diffraction breadths of the 120, 201 and 004 $\text{CuK}\alpha$ x-ray reflections from boron nitride. $\beta(2\theta)$ is defined as $2\int I(\theta)d\theta/I_{\max}$, where θ is the Bragg angle and $I(\theta)$ is the intensity distribution.

photographs of irradiated BN. These non-saturating effects were attributed to two possible causes: the steady destruction of ^{10}B atoms, and the creation of relatively large volumes so heavily disordered that the saturating mechanism can no longer operate. Tucker and Senio (1954) irradiated single crystals of B_4C

and report striking changes in the x-ray patterns which are qualitatively the same at all doses up to 3×10^{20} slow neutrons cm^{-2} (0.2 BPPA), for which dose they report results. This dose is over a hundred times the dose to half-saturation and it therefore appears that Tucker and Senio were measuring non-saturating effects. At this dose, approximately 13% of the boron atoms were destroyed and replaced by 20% of lithium and helium impurities. This would probably be sufficient to account for the effects reported. Further, although each atom of the structure would have been displaced about 10 times on the average, the single crystal x-ray pattern was still observable.

5.3.4. *The metamict state.*

The often observed optical isotropy of metamict minerals was long interpreted as indicating an amorphous state, and this view was confirmed by Vegard's (1916) important observation, subsequently repeated on many other metamict minerals, that metamict ThSiO_4 gave no detectable x-ray reflections in spite of a relatively perfect outward morphology. Berzelius (1815) and Wollaston discovered the striking nature of the release of stored energy in gadolinite, in which, by uniform heating of a sample, a sufficient amount of heat can be released suddenly to raise the sample to a high temperature. Faessler's (1942) measurement of the quantity of heat released (89 cal g^{-1}) shows that it was of the same order as the heat of crystallization of such substances as fused quartz. Kulp, Volchok and Holland (1952) have shown by differential thermal analysis that at low doses the stored energy in zircon and samarskite is proportional to dose. While the process of recovery is certainly a recrystallization, this is often extremely complicated, and Pabst (1952) concludes that the original single crystal can only be reconstituted when at least traces of the original lattice are still present. All metamict minerals contain uranium or thorium. These facts, together with the heavy doses we have calculated for radioactive minerals, show that the metamict state is an amorphous end-product of prolonged irradiation.

It is known, however, that not all radioactive minerals are found in the metamict state, and x-ray studies of minerals such as ThO_2 , $(\text{Th}, \text{Y}) \text{PO}_4$, UO_2 (except when weathered) and a monoclinic form of ThSiO_4 (Huttonite) show no appreciable destruction of long range order at the highest doses. The reasons for this have been a matter of speculation for a number of years (Pabst 1952, Hurley and Fairbairn 1953), and, as may be seen from the observations on the different forms of ThSiO_4 , the presence or absence of the transformation must depend critically on relatively obscure factors. Primak (1954) has pointed out that generalizations based on the degree of ionic character in the bonds (Pellas 1951, Primak, Fuchs and Day 1953) are insufficient to provide a guide.

It is clear from the discussion on the accumulation of damage and from the results of the x-ray investigations of the covalent compounds that, provided the crystal structure is maintained, the concentration of single interstitial atoms must saturate, even when there is no thermally activated recovery. For room temperature irradiations, the saturation concentration of interstitial atoms in most cases can hardly be greater than 1% or so, since this is the order of the lattice expansions observed. Thus the displacement of atoms to interstitial sites will not by itself produce the metamict state. Several possible mechanisms may be mentioned by which further disorder can be introduced: (a) the crystal structure

becoming unstable at interstitial concentrations of less than the saturation value, (b) atoms going to the wrong type of lattice site, (c) the disarrangement of relatively large volumes of material in a single event, (d) accumulation of impurities. As far as quartz and its polymorphs are concerned, suggestion (a) seems the most promising; Wittels and Sherrill (1954) have pointed out that there are grounds for supposing that α -quartz contains 'permanent damage' at doses exceeding 2×10^{19} neutrons cm^{-2} . Moreover, neither (b) nor (d) are likely to operate in this case. That naturally irradiated quartz is not metamict may be due to the relatively very slow rate of irradiation, or to the different type of radiation involved. In the case of the boron compounds, it seems likely that (d), due to the burn-up of ^{10}B , is mainly responsible for the non-saturating effects; but at least in the case of B_4C , it seems unlikely that this would produce a fully metamict state, even if all the ^{10}B were destroyed.

Hurley and Fairbairn (1953) interpreted the already-mentioned saturation of the changes in the Bragg angle of the 112 reflection from zircon, as the transformation to the metamict state. On the assumption that saturation sets in when all the atoms have been displaced once, they obtained 4500 displaced atoms for each α -disintegration. This number is rather larger than that estimated in § 4.5, which is unusual (see table 2.2), and leaves no margin for recovery of any sort. The density changes represented by the maximum change in Bragg angle is 4%. The density of fully metamict zircon measured by macroscopic methods is about 17% below that of the undamaged (and of fully annealed) material (Anderson and Payne 1937). This discrepancy can hardly be due to experimental errors, and its existence is fully confirmed by the results of earlier workers (Chudoba and von Stackelberg 1936, Lietz 1937). Further, it is difficult to see how an x-ray reflection can be obtained from a *fully* metamict sample. It therefore seems that the saturation of the Bragg angle changes is due to a saturation of the interstitial concentration in the zircon lattice, and that the transformation to the metamict state, which is superimposed on this, is a growth, either in number or in volume, of domains of amorphous material within the crystal.

5.4. Alkali Halides

The high density of colour centres and the changes in mechanical properties produced in the alkali halides by low energy radiation require the supposition that ionization introduces crystalline defects (see Seitz 1954, Varley 1954 a, b). Since charged particle or neutron irradiation is invariably accompanied by ionizing radiation, it is difficult to identify the contribution of defects formed by the atomic collision processes discussed in § 2. Studies have been made of the effects of high energy radiation on the optical absorption spectrum (Pringsheim and Yuster 1950, Casler, Pringsheim and Yuster 1950, Prizibram 1951, Westervelt 1952), conductivity (Nelson, Sproull and Caswell 1953, Pearlstein 1953, 1954), paramagnetic resonance (Hutchison 1949, Tinkham and Kip 1951), density and mechanical properties (Leivo 1953, Vaughan, Leivo and Smoluchowski 1953, Leivo and Smoluchowski 1954, Westervelt 1954, Binder and Sturm 1954). Satisfactory separation of the effects of ionization from those of collisions has not so far been made.

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REFERENCES

- ADAM, J., and DUGDALE, R. A., 1951, *Nature, Lond.*, **168**, 582.
 ADAM, J., GREEN, A., and DUGDALE, R. A., 1952, *Phil. Mag.*, **43**, 1216.
 ALLISON, S. K., and WARSHAW, S. D., 1953, *Rev. Mod. Phys.*, **25**, 779.
 ANDERSON, B. W., and PAYNE, C. J., 1937, *The Gemmologist*, **7**, 297.
 ANDRADE, E. N. DA C., 1945, *Nature, Lond.*, **156**, 113.
 ANDREW, A., and DAVIDSON, C. R., 1953, *Phys. Rev.*, **89**, 876.
 ARONIN, L. R., 1954, *J. Appl. Phys.*, **25**, 344.
 BARSCHALL, H. H., ROSEN, L., TASCHKE, R. F., and WILLIAMS, J. H., 1952, *Rev. Mod. Phys.*, **24**, 1.
 BARTLETT, J. H., and DIENES, G. J., 1953, *Phys. Rev.*, **89**, 848.
 BECQUEREL, H., 1901, *C.R. Acad. Sci., Paris*, **133**, 709.
 BENNY, A. H., and CHAMPION, F. C., 1954, *Nature, Lond.*, **173**, 1087.
 BERMAN, R., 1951, *Proc. Roy. Soc. A*, **208**, 90; 1953, *Advances in Phys. (Phil. Mag. Suppl.)*, **2**, 103.
 BERMAN, R., FOSTER, E. L., and ROSENBERG, H. M., 1955, Report of the Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
 BERMAN, R., KLEMENS, P. G., SIMON, F. E., and FRY, T. M., 1950, *Nature, Lond.*, **166**, 864.
 BERZELIUS, J., 1815, *Afhandl. Fys. Kem. Min.*, **4**, 217 (referred to by Pabst 1952).
 BETHE, H. A., and ASHKIN, J., 1953, *Experimental Nuclear Physics*, **1**, 166, Ed. E. Segrè (New York: Wiley).
 BILLINGTON, D. S., and SIEGEL, S., 1950, *Metal Progr.*, **58**, 847.
 BINDER D., and STURM, W. J., 1954, *Phys. Rev.*, **96**, 1519.
 BINNIE, W. P., and LIEBSCHUTZ, A. M., 1954, *Phys. Rev.*, **94**, 1410.
 BLEWITT, T. H., and COLTMAN, R. R., 1951, *Phys. Rev.*, **82**, 769; 1952, *Ibid.*, **85**, 384; 1954, *Acta Metallurgica*, **2**, 549.
 BOHR, N., 1948, *K. Danske Vidensk. Selsk. Mat. Fys. Medd.*, **18**, 8.
 BOWEN, D. B., EGGLESTON, R. R., and KROPSCHOT, R. H., 1952, *J. Appl. Phys.*, **23**, 630.
 BOWEN, D., and RODEBACK, G. W., 1953, *Acta Metallurgica*, **1**, 649.
 BRADLEY, R. C., 1954, *Phys. Rev.*, **93**, 719.
 BRATTAIN, W. H., and PEARSON, G. L., 1950, *Phys. Rev.*, **80**, 846.
 BRIGGS, G. H., 1954, *Rev. Mod. Phys.*, **26**, 1.
 BRINKMAN, J. A., 1954, *J. Appl. Phys.*, **25**, 961.
 BRINKMAN, J. A., DIXON, C. E., and MEECHAN, C. J., 1954, *Acta Metallurgica*, **2**, 38.
 BROEGGER, W. C., 1893, *Salmonsens store illustratede Konversationslexicon*, **1**, 742. (Abstract in *Z. Kristallogr.*, 1896, **25**, 427)
 BROOM, T., 1954, *Advances in Physics, (Phil. Mag. Suppl.)* **3**, 26.
 BROWN, C. S., and THOMAS, L. A., 1952, *Nature, Lond.*, **169**, 35.
 BROWN, W. L., FLETCHER, R. C., and WRIGHT, K. A., 1953, *Phys. Rev.*, **92**, 591.
 BURTON, M., 1947, *J. Phys. Chem.*, **51**, 611.
 CASLER, R., PRINGSHEIM, P. and YUSTER, P., 1950, *J. Chem. Phys.*, **18**, 887.
 CHARLESBY, A., 1954, *Nucleonics*, **12**, No. 6, 18.
 CHIPMAN, D. L., WARREN, B. E., and DIENES, G. J., 1953, *J. Appl. Phys.*, **24**, 1251.
 CHOONG, S. P., 1945, *Proc. Phys. Soc.*, **57**, 49.
 CHUDOBA, K., and VON STACKELBERG, M., 1936, *Z. Kristallogr.*, **95**, 230.
 CLELAND, J. W., BILLINGTON, D. S., and CRAWFORD, J. H., 1953, *Phys. Rev.*, **91**, 238.
 CLELAND, J. W., and CRAWFORD, J. H., 1954a, *Phys. Rev.*, **93**, 894; 1954b, *Ibid.*, **94**, 1410; 1954c, *Ibid.*, **95**, 1177.

- CLELAND, J. W., CRAWFORD, J. H., LARK-HOROVITZ, K., PIGG, J. C., and YOUNG, F. W., 1951a, *Phys. Rev.*, **83**, 312; 1951b, *Ibid.*, **84**, 861.
- CLELAND, J. W., LARK-HOROVITZ, K., and PIGG, J. C., 1950, *Phys. Rev.*, **78**, 814.
- COLTMAN, R. R., and BLEWITT, T. H., 1953, *Phys. Rev.*, **91**, 236.
- COOK, L. G., and CUSHING, R. L., 1953, *Acta Metallurgica*, **1**, 539.
- COOPER, H. G., KOEHLER, J. S., and MARX, J. W., 1954, *Phys. Rev.*, **94**, 496.
- CORK, J. M., 1942a, *Phys. Rev.*, **62**, 80; 1942b, *Ibid.*, **6**, 318.
- CRAWFORD, J. H., CLELAND, J. W., HOLMES, D. K., and PIGG, J. C., 1953, *Phys. Rev.*, **91**, 243.
- CRAWFORD, J. H., and LARK-HOROVITZ, K., 1950, *Phys. Rev.*, **78**, 815.
- DAINTON, F. S., and ROWBOTTOM, J., 1954, *Trans. Faraday Soc.*, **50**, 480.
- DAVIS, R. E., JOHNSON, W. E., LARK-HOROVITZ, K., and SIEGEL, S., 1948, *Phys. Rev.*, **74**, 1255.
- DAY, H. R., 1953, *Phys. Rev.*, **91**, 822.
- DENNEY, J., 1953, *Phys. Rev.*, **92**, 531; 1954a, *U.S. AEC Report NAA-SR-271*; 1954b, *Phys. Rev.*, **94**, 1417.
- DEXTER, D. L., 1952, *Phys. Rev.*, **87**, 768.
- DIECKAMP, H., and CRITTENDEN, E. C., 1954, *Phys. Rev.*, **94**, 1418.
- DIENES, G. J., 1952a, *Phys. Rev.*, **86**, 228; 1952b, *Ibid.*, **87**, 666; 1953a, *Ann. Rev. Nuclear Sci.*, **2**, 187; 1953b, *J. Appl. Phys.*, **29**, 666; 1953c, *Phys. Rev.*, **91**, 1283.
- DITCHBURN, R. W., MITCHELL, E. W. J., PAIGE, E. G. S., CUSTERS, J. F., DYER, H. B., and CLARK, C. D., 1955, Report of Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
- DIXON, C. E., and BOWEN, D. B., 1954, *Phys. Rev.*, **94**, 1418.
- DIXON, C. E., and MEECHAN, C. J., 1953, *Phys. Rev.*, **91**, 237.
- DIXON, C. E., MEECHAN, C. J., and BRINKMAN, J. A., 1953, *Phil. Mag.*, **44**, 449.
- DUGDALE, R. A., 1952, *Phil. Mag.*, **43**, 912; 1953, *Brit. J. Appl. Phys.*, **4**, 337; 1955, Report of Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
- DUGDALE, R. A., and GREEN, A., 1954, *Phil. Mag.*, **45**, 163.
- EGGEN, D. T., and LAUBENSTEIN, M. J., 1953, *Phys. Rev.*, **91**, 238.
- EGGLESTON, R. R., 1953, *Acta Metallurgica*, **1**, 679.
- EGGLESTON, R. R., and BOWMAN, F. E., 1953, *J. Appl. Phys.*, **24**, 229.
- EHRMANN, M. L., 1950a, *Gems*, **6**, 295; 1950b, *Ibid.*, **6**, 318.
- FAESSLER, A., 1942, *Z. Kristallogr.*, **104**, 81.
- FAN, H. Y., and LARK-HOROVITZ, K., 1955, Report of the Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
- FILLNOW, R. H., HALTEMAN, E. K., and MECHLIN, G. F., 1953, *Phys. Rev.*, **91**, 236.
- FLEEMAN, J., 1953, *Phys. Rev.*, **91**, 237; 1954, *Ibid.*, **94**, 1422.
- FLETCHER, R. C., and BROWN, W. L., 1953, *Phys. Rev.*, **92**, 585.
- FLORIDA, C. D., HOLT, F. R., and STEPHEN, J. H., 1954, *Nature, Lond.*, **173**, 397.
- FORMAN, G., 1949, *Phys. Rev.*, **76**, 196.
- FORSTER, J. H., FAN, H. Y., and LARK-HOROVITZ, K., 1952, *Phys. Rev.*, **86**, 643; 1953, *Ibid.*, **91**, 229.
- GEIB, I. G., and GRACE, R. E., 1952, *Phys. Rev.*, **86**, 643.
- GLICK, H. L., BROOKS, F. C., WITZIG, W. F., and JOHNSON, W. E., 1952, *Phys. Rev.*, **87**, 1074.
- GLICK, H. L., and WITZIG, W. F., 1953, *Phys. Rev.*, **91**, 236.
- GRIFFITHS, J. H. E., OWEN, J., and WARD, J. M., 1954, *Nature, Lond.*, **173**, 439; 1955, Report of Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
- GROVE, W. R., 1852, *Phil. Trans. Roy. Soc.*, **142**, 87.
- HAHN, O., 1936, *Applied Radiochemistry* (Ithaca: Cornell U.P.).
- HAMBERG, A., 1914, *Geol. Fören. Stockh. Förh.*, **36**, 31 (referred to by Pabst, 1952).
- HAMILTON, J. G., PUTNAM, T. M., and EHRMANN, M. L., 1952, *Amer. Min.*, **37**, 941.
- HARDY, J. A., 1949, *Gems*, **6**, 167.
- HAYES, S., and SMOLUCHOWSKI, R., 1953, *Phys. Rev.*, **91**, 244.
- HUANG, K., 1947, *Proc. Roy. Soc. A*, **190**, 102.
- HUFFMAN, J. R., 1954, *Nucleonics*, **12**, No. 4, 20.
- HUNTINGTON, H. B., 1942, *Phys. Rev.*, **61**, 325; 1953, *Ibid.*, **91**, 1092; 1954, *Ibid.*, **93**, 1414.
- HUNTINGTON, H. B., and SEITZ, F., 1942, *Phys. Rev.*, **61**, 315.

- HURLEY, P. M., and FAIRBAIRN, H. W., 1952, *J. Appl. Phys.*, **23**, 1408; 1953, *Bull. Geol. Soc. Amer.*, **64**, 659.
- HUTCHISON, C. A., 1949, *Phys. Rev.*, **75**, 1769.
- JAMES, H. M., and LARK-HOROVITZ, K., 1951, *Z. phys. Chem.*, **198**, 107.
- JOHNSON, F. B., and PEASE, R. S., 1954, *Phil. Mag.*, **45**, 651.
- JOHNSON, R. D., and MARTIN, A. B., 1952, *J. Appl. Phys.*, **23**, 1245.
- JOHNSON, W. E., and LARK-HOROVITZ, K., 1949, *Phys. Rev.*, **76**, 442.
- JOLY, J., 1907, *Phil. Mag.*, **13**, 309.
- JONES, E. R. W., MUNRO, W., and HANCOCK, N. H., 1954, *J. Nucl. Energy*, **1**, 76.
- JONGENBURGER, P., 1953a, *Phys. Rev.*, **90**, 710; 1953b, *Appl. Sci. Res., Hague B*, **3**, 237.
- KEESOM, P. H., LARK-HOROVITZ, K., and PEARLMAN, N., 1952, *Science*, **116**, 630.
- KEYWELL, F., 1952, *Phys. Rev.*, **87**, 161.
- KIERSTEAD, H. A., 1954, *Bull. Amer. Phys. Soc.*, **29**, 30.
- KINCHIN, G. H., 1953, *Proc. Roy. Soc. A*, **217**, 9; 1954, *J. Nucl. Energy*, **1**, 124.
- KINCHIN, G. H., and PEASE, R. S., 1955, *J. Nucl. Energy*, **1**.
- KITTEL, C., 1953, *Introduction to Solid State Physics* (New York: Wiley).
- KLEMENS, P. G., 1951, *Proc. Roy. Soc. A*, **208**, 108.
- KLONTZ, E. E., 1952, *U.S. AEC Report*, AECU 2267.
- KLONTZ, E. E., and LARK-HOROVITZ, K., 1951, *Phys. Rev.*, **82**, 763; 1952, *Ibid.*, **86**, 643.
- KNIPP, J., and TELLER, E., 1941, *Phys. Rev.*, **59**, 659.
- KOEHLER, J. S., and SEITZ, F., 1954, *Z. Phys.*, **138**, 238.
- KUBASCHESKI, O., 1950, *Trans. Faraday Soc.*, **46**, 713.
- KULP, J. L., VOLCHOK, H. L., and HOLLAND, H. D., 1952, *Amer. Min.*, **37**, 709.
- KUNZ, F. W., and HOLDEN, A. N., 1954, *Acta Metallurgica*, **2**, 816.
- LARK-HOROVITZ, K., 1951, *Semi-Conducting Materials*, Ed. H. K. HENISCH (London: Butterworths Scientific Publications), p. 47.
- LARK-HOROVITZ, K., BECKER, M., DAVIS, R. E., and FAN, H. Y., 1950, *Phys. Rev.*, **78**, 334.
- LARK-HOROVITZ, K., BLEULER, E., DAVIS, R. E., and TENDAM, D., 1948, *Phys. Rev.*, **73**, 1256.
- LEIVO, W. J., 1953, *Phys. Rev.*, **91**, 245.
- LEIVO, W. J., and SMOLUCHOWSKI, R., 1954, *Phys. Rev.*, **93**, 1415.
- LIETZ, J., 1937, *Z. Kristallogr.*, **98**, 201.
- LIND, S. C., 1928, *Chemical Effects of Alpha Particles and Electrons* (New York: Chemical Catalog Co.)
- LIND, S. C., and BARDWELL, D. C., 1923a, *J. Franklin Inst.*, **196**, 375; 1923b, *Ibid.*, **196**, 521.
- MAKIN, M. J., 1955, *J. Nucl. Energy*, **1**.
- MARTIN, A. B., AUSTERMAN, S. B., EGGLESTON, R. R., MCGEE, J. F., and TARPINIAN, M., 1951, *Phys. Rev.*, **81**, 664.
- MARSDEN, E., 1910, *Proc. Roy. Soc. A*, **83**, 548.
- MARX, J. W., COOPER, H. G., and HENDERSON, J. W., 1952, *Phys. Rev.*, **88**, 106.
- MASSEY, H. S. W., and BURHOP, E. H. S., 1952, *Electronic and Ionic Impact Phenomena* (Oxford: University Press).
- MAYBURG, S., 1954, *Phys. Rev.*, **95**, 38.
- MCCLELLAND, J. D., and DONOGHUE, J. J., 1953, *J. Appl. Phys.*, **24**, 963.
- MCDONELL, W. R., and KIERSTEAD, H. A., 1954, *Phys. Rev.*, **93**, 247.
- McKAY, H. A. C., 1950, *Prog. Nuclear Phys.*, **1**, 168.
- McKINLEY, W. A., and FESHBACH, H., 1948, *Phys. Rev.*, **74**, 1759.
- McREYNOLDS, A. W., AUGUSTYNIAK, W., McKEOWN, W., and ROSENBLATT, D. B., 1954, *Phys. Rev.*, **94**, 1417.
- MEECHAN, C. J., and EGGLESTON, R. R., 1954, *Phys. Rev.*, **93**, 953.
- MEYER, R. A., 1954, *J. Appl. Phys.*, **25**, 1369.
- MITCHELL, E. W. J., and PAIGE, E. G. S., 1954, *Proc. Phys. Soc., B*, **67**, 262.
- MOSS, T. S., 1952, *Photoconductivity in the Elements* (London: Butterworths Scientific Publications), p. 105.
- MOTT, N. F., 1929, *Proc. Roy. Soc. A*, **124**, 425; 1932, *Ibid.*, **135**, 429.
- MURRAY, G. T., and TAYLOR, W. E., 1954, *Acta Metallurgica*, **2**, 52.
- NABARRO, F. R. N., 1952, *Phys. Rev.*, **87**, 665.
- NELSON, C. M., SPROULL, R. L., and CASWELL, R. S., 1953, *Phys. Rev.*, **90**, 364.
- NIX, F. C., and SHOCKLEY, W., 1938, *Rev. Mod. Phys.*, **10**, 1.

- O'BRIEN, M. C. M., and PRYCE, M. H. L., 1955, Report of Bristol Conference on *Defects in Crystalline Solids* (London: Physical Society).
- OVERHAUSER, A. W., 1953, *Phys. Rev.*, **90**, 393; 1954, *Ibid.*, **94**, 1551.
- OZEROFF, J., 1949, *U.S. AEC Report AEC-D 2973*.
- PABST, A., 1952, *Amer. Min.*, **37**, 137.
- PEARLSTEIN, E., 1953, *Phys. Rev.*, **92**, 881; 1954, *Ibid.*, **94**, 1409.
- PEASE, R. S., 1954, *Acta Cryst., Camb.*, **7**, 633.
- PELLAS, P., 1951, *C.R. Acad. Sci., Paris*, **233**, 1369.
- PEPPER, R., KLONTZ, E., LARK-HOROVITZ, K., and MACKEY, J., 1954, *Phys. Rev.*, **94**, 1410.
- PRIMAK, W., 1954, *Phys. Rev.*, **95**, 837.
- PRIMAK, W., FUCHS, L. H., and DAY, P., 1953, *Phys. Rev.*, **92**, 1064.
- PRINGSHEIM, P., 1953, *Phys. Rev.*, **91**, 551.
- PRINGSHEIM, P., and VORECK, R. S., 1952, *Z. Phys.*, **133**, 2.
- PRINGSHEIM, P., and YUSTER, P., 1950, *Phys. Rev.*, **78**, 293.
- PRZIBRAM, K., 1951, *Z. Phys.*, **130**, 269.
- REDMAN, J. K., COLTMAN, R. R., and BLEWITT, T. H., 1953, *Phys. Rev.*, **91**, 448.
- RANDOLPH, B., 1952, *Phys. Rev.*, **85**, 710.
- ROBINSON, W. H., LI, Y. Y., and SMOLUCHOWSKI, R., 1954, *Phys. Rev.*, **94**, 1435.
- ROSENBLATT, D. B., SMOLUCHOWSKI, R., and DIENES, G. J., 1954, *Phys. Rev.*, **94**, 1417.
- RUTHERFORD, E., 1910, *Proc. Roy. Soc. A*, **83**, 561.
- RUTHERFORD, E., CHADWICK, J., and ELLIS, C. D., 1930, *Radiations from Radioactive Substances* (Cambridge: University Press).
- SCHNEIDER, E. G., and O'BRYAN, H. M., 1937, *Phys. Rev.*, **51**, 293.
- SEITZ, F., 1949, *Disc. Faraday Soc.*, **5**, 271; 1952a, *Phys. To-day*, **5**, 6; 1952b, *Advances in Phys.*, **1**, 43; 1954, *Rev. Mod. Phys.*, **26**, 7.
- SIDHU, S. S., and HENRY, C. O., 1950, *Phys. Rev.*, **80**, 123.
- SIEGEL, S., 1949, *Phys. Rev.*, **75**, 1823.
- SISMAN, O., and BOPP, C. D., 1951, *U.S. AEC Report ORNL 928*.
- SLATER, J. C., 1951, *J. Appl. Phys.*, **22**, 237.
- SMITH, A. W., and TURKEVITCH, J., 1954, *Phys. Rev.*, **94**, 859.
- SNYDER, W. S., and NEUFELD, J., 1954, *Phys. Rev.*, **94**, 760.
- STEVENS, D. K., CLELAND, J. W., and CRAWFORD, J. H., 1954, *Phys. Rev.*, **94**, 1409.
- TAYLOR, B. T., 1952, *AERE Report No. N/R. 1005*.
- TINKHAM, M., and KIP, A. F., 1951, *Phys. Rev.*, **83**, 657.
- TOWNES, C. H., 1944, *Phys. Rev.*, **65**, 319.
- TUCKER, C. W., and SAMPSON, J. B., 1954, *Acta Metallurgica*, **2**, 433.
- TUCKER, C. W., and SENIO, P., 1954, *Acta Cryst., Camb.*, **7**, 456.
- VARLEY, J. H. O., 1954a, *Nature, Lond.* **174**, 886; 1954b, *J. of Nucl. Energy*, **1**, 130.
- VAUGHAN, W. H., LEIVO, W. J., and SMOLUCHOWSKI, R., 1953, *Phys. Rev.*, **91**, 245.
- VEGARD, L., 1916, *Phil. Mag.*, **32**, 65.
- WATT, B. E., 1952, *Phys. Rev.*, **87**, 1037.
- WELLS, H. G., 1909, *Tono-Bungay* (London: Macmillan).
- WERNER, G. K., 1954, *Phys. Rev.*, **93**, 633.
- WESTERVELT, D., 1952, *Phys. Rev.*, **86**, 643; 1954, *U.S. AEC Report NAA-SR-888*.
- WIGNER, E. P., 1946, *J. Appl. Phys.*, **17**, 857.
- WILLIAMS, E. J., 1945, *Rev. Mod. Phys.*, **17**, 217.
- WITTELS, M., 1953, *Phys. Rev.*, **89**, 657.
- WITTELS, M., and SHERRILL, F. A., 1954, *Phys. Rev.*, **93**, 1117.
- WITZIG, W. F., 1952, *J. Appl. Phys.*, **23**, 1263.
- WRUCK, D., and WERT, C., 1954, *Phys. Rev.*, **94**, 1417.
- YOCKEY, H. P., ANDREW, A., FILLMORE, F. L., GLASGOW, L. E., HUNT, C. D'A., and PEPPER, J. H., 1954, *Rev. Sci. Instrum.*, **25**, 1011.