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• G. J. DIENES
• G. H. VINEYARD

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G. J. DIENES
Department of Physics, Brookhaven National Laboratory, Upton, New York

G. H. VINEYARD
Department of Physics, Brookhaven National Laboratory, Upton, New York

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Preface

The study of radiation effects in solids is now proceeding more intensively than ever before, and the subject can be expected to develop greatly in the next few years. Nevertheless the field has already reached a certain level of maturity, and a very large set of experimental results are at hand, coordinated at least qualitatively by a body of theoretical ideas. It thus seems appropriate to bring out a small volume surveying the subject in its present state. It is not the authors' intension to extoll the accomplishments of the theory unduly. Indeed, we have emphasized its shortcomings as well as its achievements, and hope that a critical awareness of limitations of present theoretical pictures will lead most quickly to their improvement. Similarly, in the experimental realm, while summarizing the basic information that has been gathered, we have tried to point out many gaps and to reveal numerous cases where inadequate control of purity, temperature, radiation conditions, and other variables make results difficult to interpret and of uncertain generality.

The book is concerned mostly with the physics of radiation effects, not with the chemistry of such effects, and not at all with biological effects. This means that displaced atoms have been given more prominence than ionization, and that organic substances have been given far less space than other types of solids. It should be also noted that we are primarily concerned with energetic radiation, of x-ray energies and higher, and thus effects of optical, infrared and ultraviolet irradiation are omitted. Although these phenomena (luminescence, photochemistry, etc.) are unquestionably radiation effects, their study goes much farther back, they have been reviewed in many places, and the theoretical ideas involved are sufficiently different from those relevant to high-energy radiation to allow a practical separation.

The book deals mainly with fundamentals, and this means that preference is given to simple systems and to irradiations carried out under controlled and analyzable conditions. At the same time a survey is given of the more striking physical effects arising from irradiations, many of these being observed in complicated situations where theoretical understanding is difficult.

It is hoped that the treatment given will be of use to graduate students, to scientists in fields other than radiation effects, and to specialists in radiation effects who desire a broad and integrated review of the fundamentals of their field.

The writers are indebted to their colleagues in the Solid State Group at Brookhaven National Laboratory for many helpful discussions, to R. W. Powell and R. A. Meyer for aid with the section on annealing of the Brookhaven Reactor, and to Mrs. Alice Whittemore for dedicated assistance in the preparation of the manuscript.

G. J. DIENES
G. H. VINEYARD

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CHAPTER 1

Introduction

While some aspects of the interaction of various nuclear radiations with solids have been studied for many years, the very active interest in radiation effects in solids at the present time is largely the result of wartime research on nuclear reactor development. E. P. Wigner recognized in the latter part of 1942 that energetic neutrons and fission fragments, born in the fission process, would have the ability to displace atoms from their equilibrium positions. He reasoned that heavy bombardment of a solid by such energetic massive particles might lead to serious technological effects. This observation prompted an immediate program of theoretical and experimental study on the nature and magnitude of the effects to be expected. Publication of basic studies commenced in 1946, but much technological and basic information remained classified until the United Nations International Conference on the Peaceful Uses of Atomic Energy in 1955.

As may be expected, much of the early work was concerned with applied problems of interest to reactor technology. During the last decade the emphasis has changed slowly as it became clear that the study of radiation effects can lead to new and valuable insight into the properties of imperfections in solids. The relation of physical and chemical properties to the defect structure of solids has become an increasingly important part of solid-state research. Irradiation with energetic particles is a new and powerful tool in this field since a large number of defects thus can be introduced into a crystal in a reasonably well controlled manner.

During the last few years the subject has achieved a certain degree of maturity. There is a theory for the production of simple point defects, namely interstitial atoms and vacant lattice sites, by energetic particle bombardment. A number of basic experiments have been done which support the simple theory in some ways but depart from it in other respects. It has been recognized that more cooperative effects, involving a few or perhaps a large number of atoms, may be of importance, and an outline of a theory of these cooperative effects is at hand. Thus, many diverse experimental observations can be and have been correlated, although the finality of the prevailing picture is difficult to judge. It is possible that present ideas will be considerably altered as more exact theoretical work becomes available and more carefully controlled experiments are performed.

Present interpretation of the changes in the properties of solids brought about by high-energy radiation centers around the production of several types of defects in the solid by the radiation. These defects are: (*a*) vacancies, (*b*) interstitial atoms, and (*c*) impurity atoms. Each of these simple defects is described briefly below.

(*a*) *Vacancies.* Vacant lattice sites may be created by collisions of energetic particles with the atoms in a solid lattice. The energy transferred in these collisions is usually sufficient for the recoiling atom to create further vacant lattice sites by subsequent collisions. Thus, for each primary collision, a cascade of collisions resulting in vacancies is initiated.

(*b*) *Interstitial atoms.* The atoms that are displaced from their equilibrium positions in the lattice will stop in an interstitial, or non-equilibrium, position, provided they do not recombine immediately with a nearby vacancy.

(*c*) *Impurity atoms.* Impurity atoms are formed under neutron bombardment by transmutation. A special case of this is the introduction of fission products by the fission process. The effect of fission fragments is usually more pronounced than that of neutron-induced transmutation, although both mechanisms are often insignificant compared to other radiation effects.

These defects were described briefly because the whole book deals essentially with the production and nature of such defects and their relation to the physical and chemical properties of solids. In addition to simple collisions there are other important processes leading to observable radiation effects. They are (*d*) replacement collisions, (*e*) thermal and displacement spikes, and (*f*) ionization effects. These processes may be described briefly as follows:

(*d*) *Replacement collisions.* If a collision between a moving interstitial atom and a stationary atom results in ejection of the stationary atom and leaves the interstitial with insufficient kinetic energy for it to escape from the vacancy it has created, then this atom will fall into the vacancy, dissipating its kinetic energy through lattice vibrations as heat. Calculations show that for a reasonable choice of energy parameters the number of replacement collisions may exceed the number of displacement collisions. The result is the interchange of moving atoms with lattice atoms, which can lead to observable effects in polyatomic materials.

(*e*) *Thermal and displacement spikes.* A fast particle moving through a lattice, or an atom that has been hit just hard enough to vibrate with large amplitude without being displaced, will rapidly transfer energy to its neighbors, which become abnormally excited. Thus a region of material around the track of a fission fragment or knocked-on atom will be heated to a high temperature. The region of excitation expands rapidly, and at the same time there is a drastic decrease of temperature. The result is called a thermal spike, i.e., rapid heating and quenching of a small volume of the material. Calculations indicate that the duration of a high temperature of approximately 1000° K in a region involving some thousands of atoms might be 10^{-10} to 10^{-11} seconds. When the energy of the fast moving atom falls below a transition value (which depends on the atomic number) the mean free path between displacement collisions becomes of the order of the atomic spacing. Then each collision results in a displaced atom, and the end of the trail is believed to be a region containing of the order of one- to ten-thousand atoms in which local melting and turbulent flow have occurred during a very short time interval. This is called a displacement spike, and is probably important only in heavy metals.

(*f*) *Ionization effects.* The passage of charged particles or gamma-rays through a solid may cause extensive ionization and electronic excitation, which in turn lead to bond rupture, free radicals coloration, luminescence, etc., in many types of solids. These effects are most important in the various insulators and dielectrics, ionic crystals, glasses, organic high polymers, etc.

The writers believe that the scientific future of the field of radiation effects is a promising one. Such studies will provide a very valuable supplement to other methods of altering the properties of solids and the processes occurring in them. The interaction of radiation with matter is a fruitful field in itself in which much remains to be done. But perhaps more important is the fact that a new tool is at hand with which to probe the intricacies of the structure-sensitive properties of solids.

The writers' interest has been to a large extent in the fundamentals, and this is reflected in the plan of the book. By far the largest portion of the book is concerned with the theory of displacement production and the basic experiments which were designed to test the theory. This material is covered in Chapters 2 and 3. In Chapter 4 point defects and clusters of defects are discussed together with the physical property changes expected from the presence of such entities. The mobility of the crystalline defects is taken up in Chapter 5, together with the healing or annealing of radiation effects due to the recombination of defects or to their disappearance from the solid by diffusion. In Chapter 6 some special topics are treated, most of which are rather complex and cannot be interpreted in a simple way, but which are important in many phases and solid-state research. While the emphasis is on fundamentals the practical importance of various radiation effects is pointed out throughout the volume. For engineering details, however, the reader will have to consult the original literature or the appropriate review articles in various books and journals. A general bibliography is given at the end of this chapter, and each chapter, we believe, is fully supplied with references.

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CHAPTER 2

The Interaction of Radiation with Matter

2.1 Introduction

The interaction of energetic radiation with matter is a complex phenomenon, and it is useful to resolve it into primary and secondary stages, which will be discussed in that order. This analysis is based on the sequence of events following the arrival of a particle or quantum of energy, and implies nothing about the relative importance of the two stages in producing observable property changes.

The primary or direct effects consist in the displacement of electrons (ionization), the displacement of atoms from lattice sites, excitation of both atoms and electrons without displacement, and the transmutation of nuclei. Irradiation with energetic charged particles always produces primary ionization, and, depending on conditions, usually produces primary atomic displacements. Irradiation with neutrons produces ionization only as a secondary process, the primary result being atomic displacement, while irradiation with gamma-rays produces only ionization as the important primary effect, atomic displacements sometimes resulting secondarily. Nuclear transmutations can in principle be produced by any of these forms of radiation, but occur to an appreciable extent (at energies up to 10 Mev) only when certain materials of high cross section are irradiated with neutrons. In this category may be included neutron capture, (n, α) reactions in lithium and boron, and fission. Other special nuclear effects may be observed under bombardments at extremely high energies ($>$ 100 Mev), but these will not be considered here (1). Excitation of nuclear and electronic motion without permanent displacement also occurs very generally but is chiefly important as a secondary process, and it will be treated explicitly in the latter connection.

The secondary effects of the interaction of radiation with matter consist of further excitation and disruption of the structure by electrons and atoms which have been knocked on. The total number of atoms displaced in such cascades must be estimated, and this involves treating further interaction between moving charged particles and undisturbed material. The basic laws governing the secondary stages are in all cases the same as those governing the primary stage of charged particle bombardment; hence the stopping of charged particles in matter is taken up first.

2.2 Moving Charged Particles

An atom moving through matter at high energies is slowed down by numerous collisions, some of which impart appreciable energy to target atoms but most of which impart energy to individual electrons of the target. Such a moving atom would be expected to be heavily ionized when it is moving at high speeds and to acquire electrons as it slows down (2). Roughly speaking, those electrons whose orbital velocities are greater than the velocity with which the atom is moving will remain attached; those electrons which have an orbital velocity lower than that of the atom will be stripped away. This means that protons or deuterons moving with energies in the megavolt range will be completely ionized, while knock-on atoms will be only rarely ionized, except for the lightest elements. Fission fragments at birth, because of their extraordinarily high energy, carry about 20 units of net positive charge, which becomes progressively neutralized as the fragment slows down.

The collisions which the moving atom undergoes can be divided into two classes, elastic and inelastic. In an elastic collision the moving atom interacts with an atom of the target material, imparting some energy to the target atom and losing a like amount of energy (thus, the collision is elastic in the sense that the total kinetic energy of incident and struck atoms is conserved, not that the incident atom is scattered without loss of energy). In an inelastic collision, there is loss of energy because of electronic excitation. In all collisions of importance here the interaction force is the Coulomb force between nuclear and electronic charges. In elastic collisions it is sufficient to consider that the electrons partially screen the nuclear charges but play no other role; thus in these collisions the electron cloud responds adiabatically to the approach of the two nuclei and partakes of no excitation. Further discussion of this process will be given later. The inelastic collisions, on the other hand, require that electrons interact directly with the incident particle, being left in excited states after its passage.

In general, inelastic collisions are much the more frequent while the atom has high energy, and elastic collisions become more important after the atom has slowed down. The transition from inelastic to elastic behavior is not abrupt but can be fairly well fixed by the following argument: If the moving atom has a velocity much less than that of an electron in the target, that electron will usually behave adiabatically in the collision, i.e., be left without excitation. If the moving atom has a velocity equal to or greater than that of the electron, electronic excitation becomes probable. Following arguments of this type a limiting energy for ionization, E_i, can be found, such that when the moving atom has energy E less than E_i, it will not lose energy to an appreciable extent by ionization, and such that when $E \gg E_i$ the ionization losses will exceed those due to elastic collisions by a large factor. Seitz (3) suggests that, in insulators

$$E_i = {}^1/_8(M_1/m)I \qquad (2\text{-}1)$$

where M_1 is the mass of the moving atom, m is the mass of an electron, and I is the lowest electronic excitation energy, given by the low-energy limit of the main optical absorption band. In metals there is no lowest electronic excitation energy, but inelastic collisions become infrequent for atom velocities low compared to the velocity of electrons at the Fermi level. Thus, for metals one may take (4)

$$E_i = {}^1/_{16}(M_1/m)\epsilon_F \qquad (2\text{-}2)$$

where ϵ_F is the Fermi energy, given approximately by

$$\epsilon_F \cong (3\pi^2)^{2/3} a_0^2 N_e^{2/3} E_R$$

where a_0 is the Bohr radius of hydrogen ($a_0 = \hbar^2/me^2 = 5.29 \times 10^{-9}$ cm), E_R is the Rydberg energy (13.60 ev), and N_e is the number of conduction electrons per unit volume.

Most common insulators have an electronic excitation energy, I, of about 5 ev, and the Fermi energies of most metals lie between 2 and 12 ev. Consequently equations 2-1 and 2-2 reduce to a typical value of E_i, in both metals and insulators, of about ${}^1/_2 M_1/m$ (ev). Individual variations away from this typical value are by not more than a factor lying between ${}^1/_2$ and 2, which is also about the precision with which the concept of a limiting energy for ionization can be defined. This leads to the useful rule of thumb that ionization is unimportant whenever the energy of a moving atom, in kev, is less than its atomic weight, regardless of the material in which it is moving. Thus, for protons this limiting energy is about 1 kev, for deuterons 2 kev, for knock-on copper atoms 65 kev, etc.

From this rule it may be seen that the energy of fast charged particles is mostly dissipated in electronic excitation when the particles are brought to rest in matter. The specific rate of energy loss by ionization is also of interest in radiation damage studies. Theories of this are neither simple nor complete, but, for energies above E_i and below the relativistic region, the following expression for the energy loss per centimeter of path by ionization will suffice (5):

$$-(dE/dx)_e = (4\pi e^4 Z_1'^2/mv^2)\, N_0\, Z_2' \ln (2mv^2/J) \qquad (2\text{-}3)$$

Here E is the energy of the moving atom, v is its velocity, $Z_1'e$ is its charge, x is the distance which it has traversed, N_0 is the density of atoms in the medium, m is the electronic mass, J is the mean excitation potential of the electrons in the stopping material, and Z_2' is their effective atomic number. J and Z_2' can only be found approximately from theory. Z_2' is the number of electrons likely to be excited, namely the number for which the excitation energy is less than $(m/M_1)E$, and J can be well approximated as $10\ Z_2$ (ev).

The total range of the charged particle can be found by integrating expressions such as equation 2-3 and making allowance for the failure of the formula at low energies. The results are not simple, and range-energy curves for several common materials can be found in Bethe and Ashkin (5). For rough calculations, it is useful to know that, approximately, the range R of a charged particle of initial energy E is given by

$$R = CE^{\gamma} \qquad (2\text{-}4)$$

where C and γ can be empirically determined. For high, nonrelativistic energies, $\gamma \cong 2$, and γ lies between 1 and 2 in most other cases.

It has been pointed out already that the most important primary process in irradiation is the displacement of atoms. Moving charged particles produce displacements primarily by elastic collisions, interacting essentially one at a time with the stationary atoms. According to the analysis of Bohr (2) and others, it is adequate to assume that, in such collisions, the moving and stationary atoms interact with a screened Coulomb potential energy, of the form

$$V(r) = (Z_1 Z_2 e^2/r)e^{-r/a} \quad (2\text{-}5)$$

Here r is the separation of the two atoms, and a is the screening constant. At close approach equation 2.5 describes the Coulomb repulsion of the two nuclei, of charge Z_1e and Z_2e, respectively. At separations of the order of a the repulsion is lessened by the partial screening of the nuclei by the two electron clouds, and at somewhat larger separations, the screening is essentially complete. The screening radius is given by the approximate relation

$$a \cong a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2} \quad (2\text{-}6)$$

where a_0 is the Bohr radius of hydrogen.

In the energy range of present interest, it turns out that the collisions can be calculated from classical mechanics with good accuracy in most cases; a discussion will be given here in classical terms as far as possible to help the reader visualize the processes. A moving atom colliding with a stationary atom will be deflected from its course by an amount which depends on its energy and on its distance of approach, the deflection being greater for smaller energies and for closer approaches. Also the momentum, and hence the energy, transferred to the stationary atom increases as the angle of deflection increases. The probability for any given amount of energy transfer can be conveniently measured by the area of a ring-shaped region in which the path of the incident particle must lie in order for this energy transfer to occur. This area will be spoken of as the differential cross section for energy transfer. Whenever the nuclei of the two atoms approach to a distance much less than the screening radius a, the nuclear Coulomb repulsion produces most of the deflection and the collision can be calculated by ignoring the screening altogether. This problem is easily solved and leads to the familiar Rutherford scattering laws. More distant collisions are partly screened, and no simple expressions can be found for the cross sections. Simplicity sets in again for very distant collisions, which occur more nearly as if the colliding bodies were hard elastic spheres. The assumption of hard-sphere behavior has been much used in displacement calculations, although it is not really very accurate in the range in which it is applied. Everhart, Stone, and Carbone (6) have made numerical