

# **Radiation Effects in Optical Materials**

**PROCEEDINGS**

198

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## PROCEEDINGS

# Radiation Effects in Optical Materials

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**SPIE Volume 541**

**Paul W. Levy**  
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**SPIE Volume 541**

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## **RADIATION EFFECTS IN OPTICAL MATERIALS**

**SPIE Volume 541**

### **INTRODUCTION**

A number of developing technologies require an appreciable increase in our understanding of nuclear radiation and high intensity light induced radiation effects in optical devices or, more specifically, the non-metals that constitute almost all optical materials. These developing activities include fiber optics, laser fusion development, space applications and, most recently, the "star wars" Strategic Defense Initiative. Following World War II numerous (nuclear) radiation effects programs were established, but because of the interest in nuclear reactor vessels and fuels, a very large fraction of this effort was devoted to metals. Also, this era included a large color-center research effort. Thus, since color center formation is the principal radiation damage effect in optical materials, one might expect the color center literature to contain appreciable radiation damage information on crystals and glasses. Unfortunately, almost all of the publications on color centers are confined to descriptions of the atomic configuration and physical properties of each type of center. Relatively few studies were devoted to the kinetics of radiation damage (i.e., color center) formation, radiation damage mechanisms, damage annealing kinetics, dose and dose rate effects, or other radiation-related properties that are now needed to model, or evaluate, radiation damage in a very large variety of optical components. Also, such evaluations are likely to be complicated by synergisms involving combinations of laser light and other forms of radiation, e.g., X rays.

The articles in this volume are intended to provide a general review of the information on radiation effects in optical materials available in 1985. An effort has been made to provide basic information that can be applied to current problems, not information on the response of specific components. The material falls into four categories:

- Basic and/or generic information on the most important radiation damage processes—including radiation damage formation kinetics, the nature of defects, defect generation, and "hole-burning" in crystals and glasses.
- Radiation damage in fiber optics, including the effects produced by transient radiation fields and high total doses.
- High intensity light (i.e., laser) induced damage to surfaces, coatings and the interior of optical materials (bulk damage).
- Radiation effects in light sources, detectors, solar cells, and space environment effects on spacecraft surface materials.

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## **RADIATION EFFECTS IN OPTICAL MATERIALS**

SPIE Volume 541

### **Contents**

Conference Committee .....	iv
Introduction .....	v
<b>SESSION 1</b> .....	<b>1</b>
541-01 Overview of nuclear radiation damage processes: phenomenological features of radiation damage in crystals and glasses, P. W. Levy, Brookhaven National Lab. ....	2
541-02 Nature of defects and defect generation in optical crystals, R. T. Williams, Wake Forest Univ. ....	25
541-03 Nature of defects and defect generation in optical glasses, D. L. Griscom, U.S. Naval Research Lab. ....	38
541-04 Laser light-induced physical processes in optical materials: persistent spectral hole-burning, W. E. Moerner, IBM San Jose Research Lab. ....	60
<b>SESSION 2</b> .....	<b>69</b>
541-05 Overview of radiation effects in fiber optics, E. J. Friebele, K. J. Long, C. G. Askins, M. E. Gingerich, M. J. Marrone, D. L. Griscom, U.S. Naval Research Lab. ....	70
541-06 Fiber optics in transient radiation fields, P. B. Lyons, Los Alamos National Lab. ....	89
541-07 Fiber optics in high dose radiation fields, J. K. Partin, EG&G Idaho, Inc. ....	97
541-08 Laser light induced bulk damage to optics, M. J. Soileau, E. W. Van Stryland, W. E. Williams, North Texas State Univ. ....	110
<b>SESSION 3</b> .....	<b>123</b>
541-09 Effects of laser radiation on surfaces and coatings, W. H. Lowdermilk, Lawrence Livermore National Lab. ....	124
541-10 Radiation effects on light sources and detectors, C. E. Barnes, Sandia National Labs. ....	138
541-11 Radiation effects on solar cells, R. L. Statler, U.S. Naval Research Lab. ....	150
541-12 Space environment effects on spacecraft surface materials, H. K. A. Kan, The Aerospace Corp. ....	164
Author Index .....	180

***RADIATION EFFECTS IN OPTICAL MATERIALS***

**SPIE Volume 541**

**Session 1**

*Chairman*

**E. Joseph Friebele**  
**U.S. Naval Research Laboratory**

# OVERVIEW OF NUCLEAR RADIATION DAMAGE PROCESSES: PHENOMENOLOGICAL FEATURES OF RADIATION DAMAGE IN CRYSTALS AND GLASSES

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## Abstract

The principle radiation damage effects occurring in optical materials, particularly those produced by energetic particles and gamma rays, are described phenomenologically. Included is a description of the basic processes whereby radiation interacts with non-metals. Emphasized are: 1) ionization induced electron and hole formation and migration processes and, 2) the displacement and ionization damage effects that are responsible for atoms being displaced from their normal lattice positions. In nonmetals, the principal radiation damage effect produced by these processes is the creation of color centers. In turn, it is shown that the radiation induced color center formation, as well as the changes that occurs after an irradiation is terminated, are described by a particularly simple theory. Radiation damage in transparent crystals and glasses is illustrated by measurements made with unique equipment for making optical measurements during and after irradiation. One arrangement utilizes a  $^{60}\text{Co}$  gamma-ray source and the other a 3.0 MeV electron accelerator. The illustrations include: 1) Measurements on F-center formation during irradiation--and the changes that occur after irradiation--on  $\text{LiF}$ ,  $\text{NaCl}$ , and  $\text{KCl}$  synthetic crystals. 2) Studies on the radiation induced F-center and Na metal colloid formation occurring in natural rock salt ( $\text{NaCl}$ ) from potential radioactive waste repository sites. 3) The growth during irradiation and decay after irradiation of color centers in glasses irradiated at different temperatures. Lastly, the radioluminescence emitted during irradiation, as well as the absorption spectrum changes and the thermoluminescence emission that is observed when irradiated samples are heated, is illustrated by studies on natural quartz.

## Introduction

The present resurgence of interest in radiation effects in optical materials--often called radiation damage, which incorrectly implies that all radiation effects are unwanted--continues research that began in the Manhattan Project during World War II. At that time various optical devices were needed to examine reactor components in intense radiation fields, very radioactive substances, etc. It was expected and immediately confirmed that glass lens elements were darkened or "browned", the word used then, by exposure to radiation. Even today, the radiation induced coloring, or more specifically the radiation induced formation of color centers, continues to be the principle radiation induced effect in glass. Surprisingly, the WWII research provided the first indications that the browning or coloring rate could be reduced by incorporating rare earth elements into the glasses. The initial interest in preventing the radiation induced coloring continued into the late 50's and early 60's, in part because of the demand for lead-glass "hot-cell" windows that did not color. Also, in the same period a number of purely basic radiation effect studies were undertaken. The interest in radiation effects research on crystals and glasses diminished for a while and then increased as interest in various space related devices, e.g. solar cells, increased. A further increase in both nuclear particle and photon induced damage and related effects in optical materials was markedly stimulated by the current interest in laser materials, fiber optics, and radiation resistant detectors for high energy physics.

However, current and future applications involving enhanced levels of light, nuclear, and laser light, or combinations of these, will certainly require appreciable additional research. For example, a practical laser driven fusion power device, will, most likely, require laser and optical components that will be subjected to both intense nuclear radiation and laser light. The research outlined above might appear to indicate existence of an appreciable body of knowledge on radiation effects in optical materials, and, in a sense, this is true. Actually, an examination of the available literature and the existing problems make it quite obvious that research on radiation effects in optical materials, particularly at high radiation levels, is "just getting started".

Since radiation effects in optical materials must include studies on transparent or nonmetallic solids, as well as semiconductor crystals, it is prudent to ask, "Does not the extensive literature on color centers in these materials, especially the alkali-halides constitute an extensive literature on radiation effects in these substances?" The answer is, to a surprising extent, "no". The color center literature is at least 95 percent de-



voted to studies on the identification of centers and the determination of their properties. Even though x-ray and other radiation sources were usually employed to create the centers studied, only a small fraction of the published papers are devoted to studies on the kinetics and other aspects of the radiation induced coloring formation processes. In a sense, a large part of the current need for radiation effects research on optical materials is a consequence of the previous lack of emphasis on the kinetics of color center formation during irradiation.

### Interaction of radiation with solids

The various mechanisms whereby radiation interacts with matter have been understood for many years. These will be outlined, primarily to provide a background for the numerous examples included in the next sections and to point out differences that have important consequences for radiation effect mechanisms.

#### Neutral particles

The best known neutral particles important for radiation effects are energetic, i.e. fast, neutrons. Because of the copious fast neutron fluxes present in nuclear reactors, often  $10^{16}$ - $10^{17}$ /cm<sup>2</sup>/sec, radiation damage in reactor materials is important and has been, by far, the subject of the most extensive damage studies. It is essential to describe, in detail, the basic interactions between fast neutrons and solids. In as much as the neutron is not charged the initial interaction with atoms in an irradiated solid is, in almost all cases, an elastic or momentum transferring collision with a single atom. For sufficiently energetic neutrons inelastic collisions, i.e. nuclear reactions, can occur that transfer momentum to a lattice atom. Also, slow or thermal neutrons can interact with atoms, most often by undergoing a (n- $\gamma$ ) reaction, that provides recoil momentum to a single atom. If, in any of these cases, the momentum transfer is sufficient, usually the struck atom must acquire energies of at least 25 eV, the atom is displaced from its normal position in the crystal or glass lattice. Thus one atom is dislodged from the lattice but, most importantly, the recoil atom can displace many more atoms if it is sufficiently energetic. This results, in part, from the fact that it usually is charged, or ionized, while in motion. The massive, compared to the neutron, recoil atom literally "plows" through the lattice and displaces numerous atoms along its trajectory. This disrupted region, containing both vacancies and interstitial atoms, is usually referred to as a displacement spike. For example, a 1 MeV neutron will produce, on the average, a spike containing 500 displaced atoms in Al<sub>2</sub>O<sub>3</sub>. In addition to displacing atoms along its path by collision process, the charged recoil will produce copious electron-hole ionization pairs. Processes associated with ionization will be described below.

#### Charged "heavy" particles, protons, alpha particles, atoms, etc

As charged energetic particles traverse solids they give up energy and produce radiation damage in the way described above for neutron produced recoils. They undergo elastic, and rarely inelastic, displacement collisions with lattice atoms and, because they are charged, give up appreciable energy by ionization. The ratio of energy lost by collision to energy lost by ionization depends on the moving particle mass, velocity and charge. As the mass increases the ratio of displacement to ionization increases. Protons produce comparatively few displacements and appreciable ionization compared with, e.g., energetic oxygen ions which produce a relatively high ratio of displacements to ionization.

#### Electrons

For almost every radiation effect application energetic electrons and positrons can be considered equivalent. As an energetic electron passes through matter it transfers energy to the lattice, almost entirely by interacting with lattice electrons. If the interaction is sufficiently strong an electron-hole ionization pair is formed. For less strong interactions the lattice electrons are excited to produce phonons, i.e. the lattice is "heated". Roughly, the energy required to produce one ion pair is between two and three times the band gap of the irradiated solid. Or, stated in another way, between one-half and one-third of the energy transferred produces ionization pairs and the remainder phonons, i.e. heat.

Electrons can displace atoms if they are sufficiently energetic. For example, to displace a Ge atom from the Ge lattice the minimum electron energy required is about 0.67 MeV (MeV not e.V). This is the minimum energy required for the low mass electron to transfer sufficient momentum to the massive Ge atom for it to acquire the 25 eV (eV not MeV) needed to displace it from its normal lattice position.

For MeV electrons the displacement process is relatively inefficient. The instant the electron enters a substance it starts to give up energy by the ionization processes described above. Usually it is stated that the energy lost per unit path length, i.e. dE/dx, is high.

Thus a large fraction of the impinging electrons are losing energy so rapidly it is likely they will degrade to energies too low to displace a lattice atom. Nevertheless, electron irradiation studies, carried out with variable energy accelerators, are the principle method for measuring the displacement energy in solids. Surprisingly, relatively few such studies have been completed on glasses and optical crystals. Since the displacement energy is an important--if not the most important--parameter for calculating radiation damage, the lack of sufficient data on displacement thresholds make it difficult to model radiation damage in optical materials.

### Photons

The discussion of the interactions of photons with transparent solids will be divided into two parts. First, photons with energies on the order of, or less than, the band gap of the material being irradiated, e.g. energies of roughly 12eV or less. And, second, photons of greater energy.

#### Low energy (optical) photons

The interaction of photons, with energies on the order of typical band-gaps, or less, with transparent solids encompasses the usual optical absorption processes. These include: valence to conduction band transitions, absorption by transitions between levels of impurities or color centers, transitions between levels in the band gap--usually associated with defects, color centers, impurities, etc.--and the conduction or valence band. With one principle exception, optical absorption transitions usually involve only a single defect, color center, impurity etc. The major exception is any transition which releases an electron to the conduction band or a hole to the valence band, or both, as occurs when a band-gap transition creates an electron-hole ionization pair.

#### High energy photons

Photons of higher energy than those contributing to the usual optical absorption processes interact with solids in three important and one usually unimportant process. As is well known, the three usual interactions are: 1) the photoelectric effect, 2) the Compton effect, and 3) electron-positron pair formation (not to be confused with the electron-hole ion pair formation, or ionization, process). The usually unimportant process is a the low probability nuclear event initiated by a high energy photon. Under photoelectron effects are included the various "inner-shell" electron excitation and/or ejection process being studied with synchrotron radiation. It is essential to emphasize that these three processes span the entire range from a few eV to the TeV range. It must also be emphasized that energetic photons, x-rays, gamma rays, etc, do not interact with solids until they create either a photoelectron, a Compton recoil, a electron-positron pair or, rarely, a nuclear event. Most importantly, once recoil electrons (and positrons) are created they interact with solids in all ways associated with any energetic electron, produced in any manner, e.g. by an electron accelerator. In other words, the properties of electrons are independent of how they are formed. Also, photon induced damage is always produced by the recoils (except for unimportant nuclear events). This point seems to be missed by many persons who are always asking, e.g. "How can you study radiation damage created by gamma rays by using an electron accelerator?"

A second consequence of radiation damage produced by photons, particularly gamma rays, x-rays etc, must be made clear. The damage produced by gamma-rays result from a two-step process. First, the creation of a recoil and, second, the creation of vacancy-interstitial displacement pairs and ion pairs along the trajectory of the recoil. Consequently, the distribution of damage in a substance subjected only to gamma rays is controlled by the penetration of the gamma rays to the point where the recoils are produced. In other words, the distribution of damage is largely controlled by the gamma-ray absorption, not the recoil absorption. For example, in glasses and crystals the half thickness for the absorption of 1-5 MeV gamma rays is on the order of 10 cm. In contrast, the damage produced by 1-5 MeV electrons is confined to a few mm below the incident surface.

#### High energy particles

To be complete, it should be stated that the principle radiation damage effects induced by high energy particles are the same as those created by the more well-known particles. The interactions are the same, but appropriate to the charge, mass, velocity (energy), etc., of these particles. This analogy extends to nuclear events, e.g. the creation of a few prong star. Once the event has taken place the emitted particles interact with solids in a manner associated with their charge, mass, energy, etc. Of course the nucleus, i.e. the atom, in which the original nuclear event occurs is displaced from the lattice. The damage associated with these single defects is usually negligible compared to the numerous displacements and ionization related processes created by each of the charged reaction products as they move through a solid.

## The basic phenomenology of radiation damage in crystals and glasses

### The defect configuration in solids before irradiation

To discuss the processes involved in radiation damage in crystals and glasses it is useful to review the defect configuration in these materials before exposure to radiation. As is well known, a crystal can be regarded as an ideal lattice structure in which are embedded numerous (in terms of  $10^{16}$  defects/cm<sup>3</sup>-which is roughly 1 ppm) defects of different kinds. For example, vacancies, divacancies, interstitial atoms and ions, both interstitial and substitutional impurities, etc., and more extended defects such as line and screw dislocations, stacking faults etc. Important for radiation induced coloring is the fact that some of these defects are electron and/or hole traps at normal temperatures. Also defects created by radiation--which may be the same as, or different from, the defects present before irradiation--can capture, i.e. trap, ionization electrons and holes.

Similar considerations apply to glasses. They can be regarded as ideal glass lattices, consisting of network formers and modifiers, in which are embedded point defects that are close analogies to those occurring in crystals. In fact, it appears that at least one of the defects found in crystal quartz has a exact counterpart in glassy quartz. In crystal quartz the electronic structure of this defect reflects the atoms in the surrounding crystal structure. In glassy quartz the electronic structure of the same defect reflects the same atoms and, in addition, the randomness of the surrounding glassy network. Just as defects in crystals may be electron and/or hole traps, the defects in glassy structures may be charge traps. Of course, the various types of defects and impurities may exhibit other "electronic" properties. For example they can be luminescent centers, radiative and non-radiative recombination centers, etc. Analogies to the extended defects, such as dislocations, stacking faults, etc., are not normally observed in glasses.

### Ionization related processes in solids

To describe radiation damage in solids it is useful to consider separately the effects associated with the creation of electron-hole ionization pairs. In other words, it is useful to assume that ionization effects are restricted to the motion of ionization electrons and holes and that they occur independently of or separately from the motion of atoms or ions. (One important exception is described below). During irradiation the numerous ionization electrons and holes enter into several distinct processes. First, as described above, ionization electrons and holes are captured or trapped on defects classified as traps. Usually holes are trapped more quickly than electrons. However, electrons can also recombine with trapped holes and visa-versa. Often the recombination is accompanied by the emission of light, i.e. luminescence or, more properly, radioluminescence. Because recombination involves opposite sign charges the cross section, or probability, for recombination is often very much larger than the cross section for trapping. Consequently, most--99 percent or more--of the ionization induced charges undergo recombination. The remaining charges, particularly if the irradiation is terminated, remain trapped. It is these charges, trapped on defects, that constitute the color-centers which are the principal source of coloring, usually called radiation damage, in non-metals.

Radiation induced coloring can be described by simple expressions that have surprisingly wide applicability. Let  $N_i$  be the concentration of the  $i$ th type of trap,  $n_i$  the concentration of traps containing trapped charges at time  $t$ ,  $\phi$  the dose rate, and  $f_i$  the fraction of empty, or uncharged, traps converted to traps with charges (color-centers) per unit time. The quantity  $\phi f_i$  will be proportional to the ionization density or dose rate. Then the growth of color centers is given by

$$dn_i/dt = \phi f_i (N_i - n_i), \text{ or} \quad (1)$$

$$n_i = N_i(1 - e^{-\phi f_i t}) \quad (2)$$

if  $n_i=0$  at  $t=0$ , when the irradiation begins. Incidentally, this equation can be derived in a rigorous way or as a special case of more general kinetics. Equation (2) is usually referred to as a saturating exponential. It applies to a large fraction of the coloring measurements made to date, examples are given below.

In materials with a number of different kinds of electron and hole traps, e.g. one type of hole trap and a number of different types of electron traps, e.g.  $j$  different types of electron traps, the growth of color centers is often given by a similar expression

$$n = \sum_{i=1}^j N_i(1 - e^{-\phi f_i t}) \quad (3)$$

i.e. by a superposition of  $j$  saturating exponential components. Numerous examples of radiation induced coloring can be given that are described by (3), some are included below.

In crystals or glasses with a number of different types of electron and hole traps, especially if the cross section for trapping on the different types of traps are similar, the radiation induced coloring is described by more general expressions that reduce to equation (3) in a number of different approximations, e.g. when the electron-hole recombination cross sections are very large.

#### Atom displacement processes in solids

The classical displacement damage process. As indicated above, the best known radiation damage mechanism for creating defects in a solid is displacement damage. Also, this process can be initiated by photons, electrons, neutrons, and charged and uncharged heavier particles. It should be obvious that the number of defects introduced in a solid target by a constant radiation field will be proportional to the flux of bombarding particles and to the irradiation time. However, after a long irradiation the net number of defects introduced per unit time will gradually decrease. This occurs only when the vacancy and interstitial concentrations have reached very high values and the possibility of vacancy-interstitial recombination is large. In this case, usually occurring only at high dose levels, "back-reactions" cannot be neglected and the net rate that defects are introduced will diminish. However, at the start of an irradiation the number of defects introduced per unit time will be proportional to the irradiation time and the incident particle flux. In other words, the number of defects introduced by an irradiation of time  $t$  will be  $Kt$ , where the defect formation rate  $K$  is proportional to the flux. As in the case of charge trapping, the defect formation process can be considered as operating independently of other processes.

The ionization damage process. In the alkali halides and to a lesser extent the alkaline earth halides negative ion vacancies are created by a unique process called ionization damage. (There is one report indicating ionization damage also occurs in quartz.) This mechanism results from processes relating to the recombination of ionization electrons and holes. In the course of the recombination a bound electron-hole pair, or exciton, is often trapped on a negative lattice ion and, as the recombination takes place, the energy released is transferred to the negative ion in a way that causes it to initiate a (usually focused) collision sequence that leaves a vacancy at the trapped exciton site and an interstitial atom some distance from this site. The net result is a vacancy with a trapped electron, or F center, and an interstitial atom. In as much as the energy required to initiate this process is the energy required to create an ionization pair, in principle one vacancy could be created by the deposition of the 10 eV or so corresponding to the band gap energy. However, one does not expect this process to be 100 percent efficient and, furthermore, on the average, it requires 2 or 3 times the band gap energy to create an ion pair. Thus it is likely that the average minimum energy required to create one vacancy by the ionization damage process is in excess of 40 or 50 eV.

In any case, the ionization damage process can produce a very large number of defects. For example, a 1 MeV electron, incident on an alkali halide, can introduce only one defect by the displacement damage process. In contrast, a 1 MeV electron could produce  $10^5$  ion pairs which, in turn, might produce  $10^3$  or  $10^4$  vacancies. For this reason one should expect that alkali halide and alkaline earth optical components will be very susceptible to radiation damage. Also, alkaline-earth compounds will be less sensitive to ionization damage than the alkali halides but much more so than oxides such as quartz. As illustrated below, both natural and synthetic rock salt (NaCl) are particularly sensitive to radiation damage, especially when irradiated in the 100 to 200°C range. In fact, the large amount of damage observed in these crystals requires the existence of an efficient defect producing process such as ionization damage. As in the displacement damage case, the rate that defects are introduced by ionization damage will be proportional to the dose and irradiation time.

Other radiation related defect formation processes. To be somewhat comprehensive, it should be mentioned that defects may be created, or appear to be created, by processes other than those described above. Two examples will be described; they are typical but do not exhaust the known possibilities. First, in crystals and glasses, defects may exist before irradiation in a configuration that prevents them being identified as a specific defect. For example, in the alkali halides negative ion vacancies may be "coupled" to a adjacent impurity atom. During irradiation it traps an electron to become an F<sub>A</sub> center with the optical absorption properties of that center. If it subsequently separates from the impurity (the impurity and/or vacancy could diffuse away) it would become an F-center and appear, in a damage formation measurement, as a radiation induced F-center. It is likely that this process occurs in most alkali halides. As a second example consider dislocations. It is well known that defects can be generated by processes associated with dislocations. Examples are vacancies "evaporating" from jogs, defects often referred to as dislocation movement debris, etc. It is quite likely that many of these dislocation related defect generation processes will be accelerated or stimulated by radiation.

## Phenomenological equations for radiation induced coloring

First, assume that a crystal or glass lattice contains  $N_{0i}$  defects of the  $i$ th type before irradiation. Also, during irradiation the  $i$ th type of defect may be introduced at the rate  $K_i$  per unit time. Then, after the irradiation has proceeded for a time,  $t$ , the sample will contain  $N_{0i} + K_i t$  defects. Second, assume, as above, that the ionization induced processes are occurring independently of the defect formation processes. Then, if  $n_i$  is the number of defects converted to color centers at time  $t$ , the defects not converted to color centers is given by  $N_{0i} + K_i t - n_i$ . Next, if, as above, it is assumed that a constant fraction of the uncolored defects, or traps, are converted to color centers per unit time (an assumption that can be shown to apply in many cases), the equation describing the growth of color centers during irradiation is

$$dn_i/dt = f\phi(N_{0i} + K_i t - n_i) \quad (4)$$

If the number of color centers present at  $t=0$ , when the irradiation is initiated; is zero, i.e. if  $n_{0i}=0$ , then this equation becomes

$$n_i = (N_{0i} - K_i/(f\phi))(1 - e^{-f\phi t}) + K_i t \quad (5)$$

Clearly this equation contains one saturating exponential and one linear component. If  $N_{0i}=0$  at  $t=0$ , i.e. if the  $i$ th type of defect does not exist before irradiation, (5) becomes

$$n_i = K_i t - [K_i/(f\phi)](1 - e^{-f\phi t}) \quad (6)$$

Equation (6) has zero slope at  $t=0$ , rises in a concave upward fashion, and becomes linear with slope  $K_i$  at large  $t$ . In other words, it exhibits a nucleation and growth character.

Normally one considers that defects are introduced by radiation. However, there are numerous mechanisms for defects to be removed by radiation and it is likely that defects are simultaneously removed and created. Let  $N_{0i}$  be the defect concentration at time  $t=0$  and let  $p_i$  be the rate that defects are removed during irradiation. In this case one equation for defect removal is

$$\begin{aligned} dN_i/dt &= K_i - p_i t \\ \text{or } N_i &= (K_i/p_i)(1 - e^{-p_i t}) + N_{0i}e^{-p_i t} \end{aligned} \quad (8)$$

If this equation for the increasing and decreasing defect concentration is inserted in (4) one obtains for the color center growth

$$\begin{aligned} dn_i/dt &= f\phi[(K_i/p_i)(1 - e^{-p_i t}) + N_{0i}e^{-p_i t} - n_i] \\ \text{or } n_i &= A_I(1 - e^{-f\phi t}) - A_D(1 - e^{-p_i t}) \end{aligned} \quad (9)$$

where  $A_I = [1/(f\phi - p_i)][f\phi N_{0i} - K_i]$  and

$$A_D = [1/(f\phi - p_i)][f\phi N_{0i} - (f\phi/p_i)K_i] \quad (10)$$

Equation (9) is the sum of increasing and decreasing saturating exponentials.

If more than one type of electron and hole traps are present, and if traps can be increased or decreased by radiation, then one reaches the following conclusion: During irradiation the growth of color centers, i.e. radiation damage, is likely to be described by curves that contain increasing saturating exponential components, decreasing saturating exponential components, and zero or one linear component, at least in the initial part of the growth curves where the concentration of radiation induced defects is too low for defect recombination to be detected.

## Phenomenological Equations For the Growth and Decay of Color Centers Occuring After Irradiation

Usually it is observed that the radiation induced color centers decay after irradiations are terminated. Occasionally the coloring increases immediately after irradiation and then decays and, in a few cases, it increases and remains at a higher level. These post irradiation changes can be attributed to a number of different mechanisms. The three given below are the most likely.

Thermal decay from the observed center. The most likely reason for a decrease in color-center concentration is thermal untrapping of the trapped charge. Let  $m_{i0}$  be the concentration of charge in the  $i$ th type of trap at the end of the irradiation and  $m_i$  the concentration at a time,  $t$ , after irradiation. Thermal untrapping is described by the well known equation

$$dm_i/dt = -m_i s_i e^{-E/kT} = -d_i m_i \quad (11)$$

where  $s_i$  is the pre-exponential "attempt-to-escape" frequency and  $\exp(-E/kT)$  the familiar Boltzmann factor with  $E_i$  the activation energy for thermal untrapping,  $k$  Boltzmann's constant and  $T$  the absolute temperature. For constant temperature all of the factors in the second term are constant and  $s \exp\{-E/kT\} = d$ , i.e. a constant. Thus if  $m = m_i$  at  $t=0$

$$m_i = m_{i0} e^{-d_i t} \quad (12)$$

This is the familiar exponential decay law.

Thermal decay from interacting centers with opposite sign charges. Just as charges may be released from the center being observed, opposite sign charges may be released from some other type of center. In this case, the released charges contributed to electron-hole recombination at the center being observed. The release of the opposite sign charges would be described by an equation like (12) but with different constants. Thus the decay of a center can contain one exponential component resulting from thermal release and one or more exponential components resulting from opposite sign charges being released from interacting traps.

Growth after irradiation. If the solid under study contains two or more types of traps which trap the same sign charge, it is possible for the concentration of one center to grow at the expense of the other. The mechanism is straight forward. If charges are released from one type of trap, all or part of them may be retrapped on the other trap. The release mechanism is the same as that given above, i.e. it is described by an exponential decay. The growth curve for the color centers trapping the charges is a saturating exponential.

This leads to the following: The changes occurring after irradiation are likely to contain one or more exponential decay components and one or more increasing saturating exponential components.

### Introductory literature on radiation damage

The material included in the previous section was chosen to provide the general, and/or introductory, information needed for the remainder of this paper and the other papers in this symposium. To reference each element in this part of the text would have required a very large number of citations and introduced numerous interruptions. Also, the large number of references required would be of little use to readers not familiar with radiation effects. Consequently, this section will provide general references, chosen to provide mostly introductory material useful as a starting point for more detailed study. The references for the remaining sections and, most importantly, the references in the following papers will, with few exceptions be quite detailed.

### General features of radiation damage

A concise well presented description of the basic physical processes important for understanding radiation damage in solids is contained in Chapters 1 and 2 of the recent book by Van Lint et al.<sup>1</sup> Additional details on radiation damage processes and numerous experimental measurements are given by Billington and Crawford<sup>2</sup>. Copious information on defects in solids, much of which is useful for understanding radiation effects, is contained in the Series, Point Defects in Solids, edited by Crawford and Slifkin<sup>3</sup>. The article by Sonder & Sibley<sup>4</sup>, Chapter 4 in Volume 1 of that series, describes radiation induced defects in ionic crystals. Somewhat older but still very useful is the article by Seitz and Koehler<sup>5</sup> and the book, Radiation Effects in Solids, by Dienes and Vineyard<sup>6</sup>.

### Color center literature

As mentioned above, the principle radiation effect in normally transparent solids is the formation of color centers. Most of the literature on color centers is contained in a very large number of papers distributed throughout the physics literature. The writer is not aware of an up-to-date compendium of this literature. Persons unfamiliar with color centers may find an encyclopedia type article useful<sup>7</sup>. Most texts on solid state physics contain at least one chapter on color centers. Appreciable detail is contained in books by Schulman and Compton<sup>8</sup>, Fowler<sup>9</sup> (ed.), and the Crawford and Slifkin series mentioned above<sup>3</sup>.

## Phenomenological theory of radiation induced color-center formation

The phenomenological theory of radiation damage formation, or more specifically, radiation induced color center formation, sketched above, is part of a to-be-published systematic treatment of this subject. However, large parts have been published, primarily in separate parts that apply to specific measurements. These include, studies on the coloring of  $\text{Al}_2\text{O}_3$ <sup>10</sup>, the coloring of glass<sup>11-13</sup>, and F-center formation in  $\text{KCl}$ <sup>14,15</sup> and  $\text{NaCl}$ <sup>16</sup>.

### Methods for studying the kinetics of radiation damage, primarily in insulators

Most radiation damage studies are carried out in one of two ways:

- a) Samples are measured, taken to an irradiation source, irradiated, and then remeasured. For example, the sample is measured in a spectrophotometer, removed and irradiated in a source, accelerator etc., and returned to the spectrophotometer and remeasured. This cycle may be repeated numerous times.
- b) Samples are measured during irradiation. This is the single way that one can measure radiation induced phenomena present only during irradiation. Also, only in this way can one determine meaningful concentrations of radiation induced species, e.g. color centers, that change rapidly after irradiation.

The illustrations of radiation damage in optical materials given below were made with two facilities developed to study radiation damage during irradiation and the changes occurring after irradiation.

#### The Gamma-ray Irradiation Facility

The principal non-electronic components in the facility for making optical absorption, luminescence and other measurements during gamma-ray irradiation are shown in Fig. 1. All radiation sensitive equipment is outside of the walk-in irradiation chamber. The data taking and control functions are performed by a DEC 11/34a computer. At the moment this facility is being modernized, primarily by replacing the original electronics with state-of-the-art equipment. The gamma-ray facility is very useful for measurements requiring long irradiations and for studies requiring a constant radiation level. It is not normally realized that a gamma-ray source is an exceedingly constant radiation device. Also, although the illustrations given below are primarily absorption and luminescence measurements, this facility has been used for a large variety of other measurements, including animal irradiations.

With the present source the dose rate at the sample can be varied from about  $10^2$  to  $10^4$  rad/hour. Data can be obtained in different ways. For example, repeated spectra can be recorded, with each spectra containing from 100 to 500 points in the range 220 to 850 nm. Alternatively, data can be rapidly recorded at a few points.

#### The Electron-Accelerator Irradiation Facility

The major non-electronic components in the facility for making optical, and other, measurements during 0.5-3.0 MeV electron irradiation is shown in Fig. 2. All data recording and control functions utilize a separate DEC 11/34a computer. This facility is also being upgraded. It is particularly useful for short irradiations, a few seconds to 8 or 10 hours, at high irradiation levels, e.g.  $10^4$  to  $10^9$  rad/hour. This facility can also be operated in a pulse mode. Usually it is operated by simultaneously recording separate 256 point absorption and radioluminescence spectra, as often as every 40 seconds, in the wavelength range 200 to 400 nm or 400 to 800 nm. In both facilities, measurements can be made at controlled temperatures between liquid helium temperatures and 900°C.

### Examples of radiation damage, particularly radiation induced coloring, in crystals and glasses

As mentioned above, the major radiation damage effect in crystals and glasses that is important for optical applications is the radiation induced coloring. The color center formation in these two classes of materials is similar in some respects and quite different in others. Included below are examples in both types of materials. They have been chosen to illustrate the overall phenomenology, not the detailed mechanisms. This is in keeping with the simple phenomenological theories of color center formation outlined above. Other papers in this symposium will provide details and mechanisms for many of the measurements described below.

LiF F-center formation and luminescence

The absorption and luminescence of LiF, measured during irradiation with 1.5 MeV electrons at room temperature, using the equipment shown in Fig. 2, is shown in Fig. 3. The measurements are in the wavelength range 200 to 400 nm (6.18 to 3.08 eV). Successively recorded absorption and luminescence spectra are shown. The upper plot shows the growth of the F-center absorption, both during irradiation and after the irradiation was terminated. The lower plot shows the radioluminescence observed during irradiation and the weak phosphorescence observed after irradiation. More details, from a similar measurement, are shown in Fig. 4. The absorption at the peak of the F-band (5.00 eV) increases during irradiation, appears to remain constant during the interval when the irradiation is interrupted, and increases when the irradiation is resumed. The luminescence, or more properly the radioluminescence, (4.15 eV) increases as the radiation progresses. After the irradiation is terminated a weak, rapidly decreasing, phosphorescence is observed. When the irradiation is resumed the luminescence, which is at a slightly reduced level from that observed when the irradiation is interrupted, increases slightly to a maximum and then decreases. More extensive measurements, made without interruptions, shows that the LiF luminescence rapidly increases to a maximum and then decreases slowly to a constant, or extremely slowly decreasing, level.

In Fig. 3 and 4 the F-center absorption appears to be constant after the irradiation is terminated. Actually it will decrease a few percent over several days. The radiation induced F-center absorption in LiF at room temperature is atypical. It is one of the few substances studied to date not exhibiting large or clearly discernable absorption changes immediately after the irradiation is terminated. This point will be clearly demonstrated in examples given below.

F-center growth and decay in KCl

The Gamma-ray Irradiation Facility has been used to make a careful study of the growth during irradiation and the decay after irradiation of F-centers in KCl.<sup>14</sup> Synthetic melt grown KCl crystals were irradiated at a dose rate of approximately  $10^5$  rad/hour and at room temperature. The absorption at the peak of the F-band was measured at closely spaced intervals. The F-center growth during irradiation is shown in Fig. 5. The insert shows the difference between the data points and the extrapolation of a "best-fit" line through the data at large irradiation times where the growth is strictly linear. This difference curve has been resolved into three saturating exponential components using a best-fit procedure. Thus, the radiation induced F-center growth in KCl is quite precisely described by the equation,

$$\alpha_F(t) = \alpha_L t + \sum_{i=1}^3 \alpha_{F0i} (1 - e^{-a_i t}) \quad (13)$$

i.e., the growth is accurately described by an expression containing one linear component and three saturating exponential components.

When the irradiation was terminated the KCl F-centers decayed monotonically. The decay, as a function of time after irradiation, is shown in Fig. 6. Actually, only the decay occurring during the first  $3.5 \times 10^4$  sec is shown. The decay was recorded to  $3.3 \times 10^5$  sec and is linear (on the semi-log plot) beyond  $1.5 \times 10^4$  sec. The extrapolation of the linear part is the upper solid line in Fig. 6. Thus, the decay after irradiation is accurately described by the expression

$$\alpha_F(t) = \sum_{i=1}^4 \alpha_{Fi} e^{-d_i t'} \quad (14)$$

where  $t'$  is the time after the irradiation is terminated and  $d_i$  is the decay constant of the  $i$ th component. In other words, the decay after irradiation is accurately described by the sum of four exponentially decaying components. Additional details are given in reference 18. These observations, and others described below, are clearly in accord with the simple theory described above.

Additional insight into radiation damage in KCl--and the alkali halides in general--is provided by studies of F-center formation in crystals strained during irradiation at a constant dose rate.<sup>18</sup> Crystals, chosen for their lack of apparent strain, were irradiated in a strain machine located in the gamma-ray irradiation facility. After an initial irradiation in their unstrained or pristine state, they were strained varying amounts in a short time. During the prestrain, strain and post strain periods the F-center level was continuously



measured. Typical F-center absorption vs. irradiation time curves are shown in Fig. 7 for KCl crystals strained varying amounts. The prestrain curves were so similar only one, for 0.25 percent strain, is shown. The changes occurring during strain are interesting and complicated but have not been studied in detail.

A number of effects are illustrated by Fig. 7. First, the F-center formation rate is not altered by a strain of 0.25 percent. Second, the F-center formation rate increases with increasing strain for strains of at least 0.5 percent or larger. It may increase for strains between 0.25 and 0.5 percent. Third, the larger the strain the smaller, percentage-wise, the rapid decay occurring after the irradiation is terminated. Fourth, the character of the F-center growth curve after strain is different from that occurring before strain. This is illustrated by Fig. 8, which shows an analysis of the 2.15 percent curve in Fig. 7. This analysis shows that the growth curve contains two saturating exponential components, not the three components observed during the initial growth preceding the strain. In other words, the growth curve shown in Fig. 8 contains two components, not the three components illustrated by Fig. 5.

This is a significant observation. One of the mechanisms contributing to F-center formation has been eliminated by: 1), straining the crystal, or 2), by virtue of the fact that the after-strain growth curve is a second opportunity for the growth mechanisms to operate. For example, consider that one of the coloring components is attributable to vacancies coupled to impurities prior to irradiation. During the initial irradiation all, or a very large fraction, of these vacancies could have been converted to F-centers that diffused away from the impurities. Thus, this source (mechanism) for F-center formation was not available after strain and consequently the number of components is reduced. There are numerous possibilities for explaining the other components. Because of space limitations only a few are mentioned here. First it cannot be assumed that the two exponential components observed after strain correspond to any of those observed prior to strain. However, since the major defect related property associated with strain is dislocation generation and movement, it is likely that one or more of the pre-strain and after-strain components are related to vacancies originating at dislocations. They could correspond to vacancies in dislocation debris, vacancies "evaporated" from jogs (this is a likely explanation for part of the linear component--which could contain a number of unresolved components), vacancies separated from impurities, etc. A fifth conclusion is contained in Figs. 7 and 8 which becomes apparent upon inspection. The slope of the linear component increases with increasing strain. This is in accord with the dislocation related processes mentioned above.

Two conclusions should be stressed. First, the KCl F-center growth curve data appears to be in good agreement with the phenomenological theory given above. Second, it is apparent that studies on radiation induced color center formation in the alkali halides can provide much useful information on radiation damage mechanisms, the relation between radiation induced processes and dislocations, and numerous other defect related properties of solids.

#### The importance of making measurements using interrupted irradiations

As mentioned above, almost all radiation damage studies are made by making measurements on a sample, irradiating it some time later and, at an even later time, repeating the original measurements. This process may be repeated numerous times. That a procedure of this kind may obscure the observation of physical processes, or even lead to misleading conclusions, is demonstrated by the measurements described in Fig. 9, 10, and 11. The sequence used to obtain the data shown in Fig. 9 was designed to emulate the usual radiation damage measurement outlined above, but in a simplified manner. The radiation induced F-center absorption was measured in the  $^{60}\text{Co}$  gamma-ray irradiation facility, at room temperature and at a constant dose rate of roughly  $10^5$  rad/hour, as the sample was alternately exposed to 30 minute irradiations and 30 minute interruptions of radiation. As shown by Fig. 9, during the first irradiation the F-centers increased monotonically, as described above. At the end of 30 minutes the gamma rays were "shut-off" and the F-centers decayed monotonically, again in accord with previous studies. During subsequent irradiations and interruptions the F-centers increased during irradiation and decreased during interruption. A growth curve of the type obtained when measurements are made in the usual manner is shown in Fig. 9. It is similar to those given in many articles, it clearly does not describe the growth process in the most meaningful way, and would not be so "smooth" if the on and off periods were not precisely controlled.

A much more involved sequence of changes in F-center concentration occurs when the same "on-off" measurements are made on melt-grown synthetic NaCl.<sup>16</sup> In this crystal continuous irradiation creates F-center growth that is very similar to that in KCl. The growth is a superposition of one linear and three saturating exponential components. However, the changes produced by an on-off irradiation are markedly different from those obtained with KCl. Details are shown in Fig. 10. Only the major features will be described. Initially, the F-centers increase monotonically, and remain roughly constant when the irradiation is interrupted. The changes occurring at higher doses, when the irradiation is interrupted or re-