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The Use of Color Centers for the Detection and Measurement
of Radiation Induced Defects*

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ABSTRACT

When materials are subjected to irradiation by energetic particles, e.g., fast neutrons, the primary radiation damage event is the formation of vacancies, interstitials, and more complex defects along the trajectory of the recoil lattice atoms. In addition, defects are formed by purely ionizing radiations such as gamma rays. Several different mechanisms have been proposed to account for this type of defect formation and these are discussed. One of the fundamental problems of radiation damage is to determine the various types of defects formed, their concentration, spatial distribution, rate of formation, etc., and how the properties of each type of defect depends on parameters such as the energy of the recoiling atom, the sample temperature, etc. In non-metals some of these defects are, or can be, converted into centers that absorb light, or color centers. Each of these centers gives rise to different optical absorption bands and from absorption measurements the center or defect concentration can be computed. Unfortunately, in many crystals numerous absorption bands have been found that have not been unequivocally attributed to specific defects. In order to use this technique to determine defect concentrations accurately, it is essential to insure that all, or a known fraction of the defects, have captured electrons or holes. In many instances the conditions required to do this can be determined by studying the conversion of existing defects into color centers by purely ionizing radiation, such as x-rays. The techniques described in this paper have been used to show that the number of defects produced in NaCl by fast reactor neutrons is consistent with existing theories on radiation damage. Also, they have been used to study the growth and annealing of the defects formed in Al_2O_3 and fused silica by reactor irradiations.

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I. Introduction - Some General Aspects of Radiation Damage.

When substances are bombarded in a reactor, they are subjected to radiations which can be divided into the two categories of ionizing radiations and particle radiations. The effects which these radiations produce are usually referred to as radiation damage, which incidentally, incorrectly implies that they are always deleterious. For most practical purposes it is the macroscopic effects that enter into practical considerations. For example, the electrical resistance of many metals increases when they are exposed in a reactor. This increase is large when the irradiations are carried out at room temperature, but is even larger when irradiations are made at liquid nitrogen temperatures (78°K). For engineering purposes it is, perhaps, sufficient to know the resistance increase in a given metal as a function of dose for various irradiation temperatures. However, to understand this phenomena it is essential to know what the irradiation has done to the metal to cause the resistance increase. Is the resistance change produced by the bombarding particles alone? Does the ionizing radiation also cause an increase in resistance? Or does the ionizing component reduce the effect of the particle component? To have a complete understanding of the radiation induced changes, one would like to have a detailed picture of radiation effects in terms of crystal structure and how it is modified by radiation. There are many other well-known radiation induced effects which we could use as illustrations of macroscopic radiation effects. These include: reactor induced changes in stress-strain curves, creep behavior, swelling of uranium, etc.

So far, only metals have been mentioned. The principal non-metal used in reactor construction is graphite. The radiation induced expansion and the concomitant energy storage of this material is well known.¹ The reduction of this expansion and the release of part of the stored energy by raising the graphite temperature has become part of the "standard operating procedure" for some

graphite reactors. But again, this is a phenomenon that is describable in terms of macroscopic changes, and is not well understood in terms of configurations of individual carbon atoms, electrons, etc., that constitute the individual crystallites of graphite.

Crystalline quartz and its amorphous counterpart glassy quartz - or fused silica (the chemical formula SiO_2 applies to both) are two non-metals that have been the subject of extensive radiation damage studies. Primak et. al.² has shown that, as a function of fast neutron dose, the density of crystal quartz decreases and that of fused silica increases. After exposure to fast neutron doses of roughly 10^{21} nvt, both materials have the same density. Primak has proposed mechanisms which explain this phenomena and the reversal of the radiation induced density changes that occur when irradiated specimens are heated. This paper will consider in detail another phenomenon which occurs when either crystal or glassy quartz is irradiated; namely, they invariably change color. This is well known to everyone who has encapsulated samples for irradiation in fused silica or any other glass. This coloring apparently occurs in all non-metals. In fact, it is difficult to bring to mind one non-metal, with the possible exception of TiO_2 , that cannot be colored by radiation under one circumstance or another. This radiation induced coloring is, in most instances, due to the formation of color centers. It is the use of color centers to determine basic radiation damage information that is discussed in this article.

II. Radiation Damage Processes.

Color centers involve individual atomic defects in the crystal lattice, individual impurity atoms, or in some instances both. Before summarizing their properties, it is exceedingly useful to describe the various radiation damage processes with emphasis on the atomic defects formed. Also, the difference between ionization and displacement^{of}/atoms must be clearly differentiated

in order to obtain an understanding of how these two processes are involved in the formation of color centers by radiation.

IIa. The Normal Ionization Process.

First, recall that when photons, e.g., gamma rays, interact with matter, the dominant process is the transfer of energy to one (or occasionally more) electrons. For visible light this energy transfer is a few electron volts, for x-rays from 10 ev to perhaps 100 kev, and for gamma rays up to several Mev. This transfer of energy from quanta to electron occurs via the photoelectric effect, Compton effect, or by pair production. These energetic electrons give up most of their energy by forming very many ionization electrons in the substance they are passing through. Obviously, energetic electrons that result from nuclear events, such as beta-ray emission, similarly create numerous ionization electrons. In ionic crystals ionization results in electrons being excited to the conduction band leaving behind an electron deficiency in the filled or valence band called a hole. These ionization electrons move about the conduction band until they are trapped on a crystal defect, such as an impurity or others which will be described below, or they recombine with a hole in the valence band. In metals ionization electrons quickly lose energy to become indistinguishable from the normal conduction electrons. In organic substances the mobility of ionization electrons is low and ionization may result in many electrons being raised to excited states of the molecules that make up the crystal. The essential fact is that only electron and hole motion is involved in the NORMAL ionization process, never atom motion.

IIb. Ionization Processes that Produce Defects.

Some ionization processes can result in atom motion in or from the bombarded substances. Undoubtedly, the best known process in this category is

photolysis. In any intense radiation field this occurs to some extent. A material that is susceptible to photolytic decomposition by x-ray and ultra-violet light, will decompose in a gamma-ray field, etc.

The ionization from gamma rays, recoil electrons, etc. usually results in the removal of only one electron from atoms in the irradiated substances, i.e., only singly ionized atoms are formed. The consequences of a small number of atoms becoming doubly ionized were first considered by Varley,³ who postulated that double ionization could cause the formation of defects by, what is now called, the Varley mechanism. Doubly ionized atoms can be formed in two ways. First, a singly ionized atom may be further ionized if a second ionization event occurs very shortly after and near enough to, the event that formed the singly charged ion. The second process that forms doubly charged ions is the Auger effect. If an inner shell electron is ejected from an atom, it may emit several x-rays in the process of restoring its electron arrangement. There is a small but finite possibility that two, or even three or more, of these x-rays will each eject outer shell electrons to form a doubly ionized atom. To illustrate what happens to a doubly charged atom in a solid, consider the case of a doubly ionized Cl atom in a NaCl crystal. Recall that each Cl^- ion is surrounded by six Na^+ ions. Removal of one electron from a Cl^- converts it to neutral Cl (Cl^0) and when a second electron is removed it becomes a positively charged Cl^+ . Obviously, this Cl^+ , which is a very small ion, is in a very unstable position since it is surrounded by positive Na^+ ions. This instability is relieved by the Cl^+ being "squirted out" of its electrostatic cage leaving behind a chlorine ion vacancy. If the ejected Cl^+ moves far enough from its original site, and reverts to Cl^0 or even Cl^- quickly enough, it cannot easily return and a stable interstitial-vacancy pair is formed.

A second mechanism whereby defects are formed by purely ionization radiation has been proposed by Crawford and Nelson.⁴ In any crystal there will be some positive ion vacancies; they may be the result of thermodynamic requirements, the presence of divalent impurities such as Ca^{++} , or evaporated from dislocations, etc. Each of these positive ion vacancies will be surrounded by six negatively charged Cl^- ions. When the crystal is subjected to ionizing radiation numerous positively charged holes will be formed. These holes can move through the crystal, and will be attracted by the positive ion vacancy. When a hole interacts with the vacancy its positive charge will neutralize one of the negative Cl^- atoms forming a neutral chlorine atom. The neutral chlorine atom is very small and can enter the positive ion vacancy leaving behind a negative ion vacancy. Furthermore, the hole- Cl^- reaction will release a certain amount of energy which can be the driving force for the newly formed negative ion vacancy to diffuse away from the vicinity of the original defect. This will leave behind a neutral chlorine atom which can combine with one of the Cl^- ions to form a Cl_2^- molecule ion (or perhaps with two Cl^- ions to form a Cl_3^- molecule ion). If the crystal is subject to further ionizing radiation, the newly formed negative ion vacancy will ultimately capture an electron to become an F-center. This process may be expected to continue as long as positive ion vacancies are present. It is conceivable that the positive ion vacancies will be replenished as fast as they are used up, and in this circumstance the rate of formation of F-centers will depend on the positive ion concentration. If, however, the positive ions are used up, the Crawford and Nelson mechanism may be expected to operate most effectively when a crystal is first exposed to ionizing radiation and to gradually become less efficient. In contrast, the Varley mechanism may be expected to occur with constant effectiveness during the entire irradiation.

The formation of vacancies and interstitials from dislocations, particularly by dislocation motion, is now generally understood. Also, it has been postulated that ionizing radiation will cause defects to be evaporated from dislocations. Obviously, the number of defects formed by these mechanisms should be dependent on the dislocation density. The maximum rate of formation of vacancies from the combined effects of all of the ionization dependent mechanisms can be determined from experiments now in progress. Also, from these measurements, it may be possible to differentiate between the various mechanisms. Some aspects of this work will be discussed below.

IIc. The Displacement of Atoms by Radiation.

Although the direct displacement of atoms by various radiations is a well known phenomena, certain aspects of it will be described here to emphasize the difference between direct displacement and the indirect or photolytic processes described above.

The simplest direct displacement results from elastic or billiard ball collisions between energetic electrons and lattice atoms. A well defined minimum energy, the displacement energy, must be transferred to the atom to move it from its normal lattice position to the closest interstitial position where it will be stable. The displacement energy is dependent on the crystallographic direction taken by the recoil atom and should vary somewhat from crystal to crystal.⁵ In most materials the directional effect can be ignored, the displacement energies vary from 15 to 50 ev, with a value of 25 ev applicable in most instances. For example, the minimum electron energy required to impart 25 ev to a Ge atom is 0.67 Mev, and, 25 ev can be imparted to a Si atom, which is much lighter, by a 0.26 Mev electron. It is essential to recall that an electron also gives up energy by ionization as it passes through matter. Thus, a one Mev electron may first give up a quarter of its energy by ionization, two-thirds in creating a displacement and the remainder in ionization. Once it is

degraded below the minimum energy required for atom displacement, it loses the remainder of its energy by ionization alone. Perhaps the next most simple phenomena that leads to displaced atoms occurs with energetic gamma rays. This is a two-step process. The first step is the formation of energetic Compton electron recoils. The second step is the formation of displacements by elastic collisions between the Compton electrons and lattice atoms by exactly the same mechanism that applies to energetic electrons described above. The energy of the Compton recoils formed by gamma rays of a given energy extend from very low energy to nearly the gamma-ray energy. Since relatively few high energy electrons are created, i.e., most of the recoil electrons are below the minimum energy required for displacements, this two-step process is relatively inefficient.

Undoubtedly, the most common radiation damage process, the one that usually comes to mind first, results from collisions between fast particles, such as neutrons, protons, etc., and lattice atoms. Neutrons interact with atoms mainly in two ways. They can make inelastic collisions that usually involve nuclear reactions - for simplicity these will be ignored - and they can make elastic, or billiard ball collisions. During an elastic collision, a large fraction of the energy of the fast neutron is imparted to a lattice atom. As the lattice atom recoil moves through the crystal it gives up energy mainly in three different ways. It increases the local vibrational motion of the lattice atoms (i.e., it causes local heating), it ionizes the lattice along its trajectory, and it makes numerous elastic collisions with other lattice atoms causing a large fraction of them to be ejected from their normal positions. A one Mev neutron can transfer sufficient energy to one lattice atom for it to produce nearly a thousand displaced atoms before it finally comes to rest. In passing through the crystal the recoiling atom leaves behind a region of displaced atoms that is roughly an elongated ellipsoid. Accompanying the recoil passage is a great deal of local heating and ionization. These are often

referred to separately as thermal spikes or ionization spikes. (There are several other kinds of spikes which will not be considered here.) The heat, ionization, and strain in each spike last only a very short time - less than 10^{-10} seconds, but each spike can cause lattice defects to be formed in addition to those created by the passage of the recoil atom. For example, if sufficient strain is developed, vacancies will be evaporated from the existing dislocations, and the additional dislocations which will be formed. This type of defect formation need not be considered in detail, but it must be made apparent that the defects formed in this way may appear to result from the recoil motion directly. This is one possible source of error in an experimental determination of the number of radiation induced defects.

As the primary radiation damage event ceases, the lattice is still in a state of violent agitation or thermal motion. This may cause a certain amount of repair or annealing of the lattice. In the hotter region of the spike all of the radiation damage may anneal away or the lattice may become completely disrupted, i.e., amorphous. In the cooler peripheral regions it is less likely that there will be a major rearrangement of lattice atoms but there should be some annealing and some coagulation of defects. Specifically, individual vacancies may combine to form divacancies or even more complicated defects. Thus, at each radiation damage event, there will be a number of defects of various kinds distributed spatially along the recoil trajectory. If the sample is kept very cold, say at liquid helium temperatures, these defects may be frozen in. However, at higher temperatures strictly thermal annealing will occur and the concentration and distribution of defects will be altered, usually in a way that will restore the perfectness of the lattice.

There are some aspects of radiation damage phenomena that should be intuitively obvious. The total number of defects produced by each incident

particle should increase, with incident particle energy. (The number of defects formed is not a linear function of bombarding particle energy.). For sufficiently large bombardments, the radiation damage regions should interact or overlap. The elastic collision, ionization, and thermal aspects of a radiation damage event may not be separable. The number and distribution of defects may depend on the sample temperature. Actually, the "state of the art" is such that only some aspects of radiation damage phenomena are susceptible to study at the present time.

Some Fundamental Problems in Radiation Damage Physics.

From the discussion above, it is apparent that certain basic scientific information on radiation damage is necessary to obtain an understanding of these phenomena. Among many questions that could be asked, the following are especially significant.

1. WHAT LATTICE DEFECTS ARE FORMED AND HOW MANY OF EACH KIND?
2. HOW DOES THE NUMBER AND CONCENTRATION OF EACH TYPE OF DEFECT DEPEND ON THE ENERGY OF THE BOMBARDING PARTICLE?
3. HOW DOES THE NUMBER AND CONCENTRATION OF DEFECTS CHANGE AS THE DAMAGED CRYSTAL IS HEATED OR ANNEALED AFTER IRRADIATION?

These questions, and some others, can be answered by making color center measurements on crystals before and after irradiation. Before describing how this can be done, some of the properties of color centers must be described.

Some Properties of Color Centers.

The classical example of a color center is the F-center most often studied in alkali-halides. Figure 1(a) is a schematic representation of a perfect portion of an alkali halide crystal such as NaCl. The plus signs represent positive Na atoms and the minus signs negative ion vacancies. A portion of crystal containing a single negative vacancy is represented by Fig. 1(b).

This region of the crystal has a net positive charge and if ionizing radiation passes near enough to it one of the electrons released may be captured by the negative ion vacancy to form an F-center as shown schematically in Fig. 1(c). NaCl crystals may contain numerous vacancies and appear perfectly colorless. When a sufficient number of negative ion vacancies have been converted to color centers by electron capture, the crystals appear colored. For example, NaCl becomes straw colored and KCl becomes purple. When the optical absorption of a colored NaCl crystal is measured with a spectrophotometer the coloring is seen to be due to a prominent optical absorption band at 4650 Å (2.66 eV). Incidentally, the name F-center comes from abbreviating the German word for color, namely farbe. Obviously, the intensity of the optical absorption band is proportional to the concentration of centers and the center concentration N can be computed by Smakula's formula

$$N = S \frac{10^{17}}{f} \frac{n}{(n^2+2)^2} U \alpha_m$$

Where N = number of color centers per cm^3 ,

S is a factor that depends on the shape of the absorption band

$S = 0.87$ for a Gaussian band,

f = oscillator strength,

n = index of refraction

U = full width of the band at half maximum in eV.

α_m = absorption coefficient = $(2.303/d)(\text{optical density})$

d = thickness of crystal in cm.

Many additional kinds of color centers are known to exist. In Fig. 1(d) two side-by-side negative ion vacancies are indicated. The same configuration is shown in Fig. 1(e) but with electrons trapped on both vacancies. This particular configuration of vacancies and charges is known as an M-center. In NaCl the peak of the M-center absorption^{band} is at 7200 Å (1.72 eV) at room temperature. A center involving a positive ion vacancy is shown in Fig. 1(f)

called a V-center. There is reason to expect that this center should also give rise to an optical absorption band. Unfortunately, in NaCl and most of the other alkali halides, it is not definitely known which, if any, absorption band corresponds to this particular center. When, for example, NaCl is colored by ionizing radiation at low temperatures, many bands are formed that have not been correlated with particular defects. In fact, at present this is the usual situation, most materials that are colored by radiation form numerous absorption bands and only a few of the bands are definitely correlated to specific defects. Thus, as our knowledge of color centers increases, they will become increasingly useful tools for identifying defects and studying their properties. Some of the simpler defects which might ultimately be identified with absorption bands are shown in Fig. 1(g).

Often color centers are formed that require the presence of certain impurity atoms. A good example of this occurs in crystal quartz. When crystals of quartz containing aluminum impurities are subjected to ionizing radiation they develop a grey coloring very similar to the color of naturally occurring crystals of smokey quartz. Similarly, naturally occurring rose quartz has recently been shown to contain Titanium impurity. Thus, it is possible that the numerous unidentified absorption bands formed by radiation in many crystals are due to the presence of impurities.

It is important to point out that ionizing radiation will cause both defects and impurity atoms to be converted to color centers. However, the number of color centers that are formed from impurity atoms must be limited to the number of impurity atoms contained in the crystal. The rate at which defects and impurity atoms are converted to color centers by ionizing radiation should be about the same for both. Once all of a specific impurity has been converted, the absorption band created should reach a fixed saturation value. If ionizing radiation causes defects to be formed this will be an inefficient

process in most instances, and the total number of defects will increase very slowly.

In the discussion above, the capture of holes and electrons by defects and impurities was described without any mention of whether or not the color centers were stable. Specifically, what is the probability that the charge which is an integral part of a color center can escape or be neutralized? Actually, this is a very difficult question to answer completely, even for one type of crystal! To a first approximation the probability that a charge can escape because of thermal motion from a color center, or any trapping center, is given by the simple expression $se^{-E/kT}$ where s is an escape frequency and ranges from 10^7 to 10^{12} per second, E is an activation energy, k is Boltzmann's constant, and T the temperature in degrees Kelvin. Thus, a center would slowly lose its charge at room temperature only if the values of s and E were to lie in a relatively narrow range. In addition to thermal untrapping, the charge on a center can be removed by recombination. This occurs when a charge of a given sign is thermally untrapped from a trapping center and migrates through the crystals until it encounters a center which contains a trapped charge of the opposite sign. For example, in an alkali halide a hole released from a V-center can recombine with an F-center electron. When this occurs, the concentration of both types of centers decreases simultaneously. The stability of color centers can be affected by other factors, but they are not important enough to require inclusion here. The stability of a particular color center at a specified temperature can be determined in a very simple way. Its concentration, i.e., the height of its absorption band, is measured over a period of time.

This discussion on the conversion of defects to color centers by subjecting crystals to ionizing radiation and the stability of color centers

after they are formed has been included to emphasize two practical considerations. First, to determine the defect concentration by converting them to color centers requires that all, or at least a known fraction, of the defects will become color centers during irradiation. Situations in which only a fraction of the centers can be converted are complicated and will not be considered here. To determine if all of a certain defect is converted usually requires a detailed knowledge of the coloring kinetics. In some instances one can demonstrate that complete conversion has been achieved by auxiliary experiments. For example, if the saturation level reached is independent of dose rate, one can assume that complete conversion has been attained, at least in a large number of cases. There is a second practical consideration which applies particularly to annealing studies. When a crystal, in which saturation coloring of a given defect occurs, is heated, optical absorption bands can be diminished by untrapping charges from the defect (leaving the defect intact), by destruction of the defect, or from both causes. For example, when a crystal is heated a vacancy can combine with an interstitial to restore the perfectness of part of the crystal lattice. In this case, two defects would be removed. Thus, it is essential to determine if any treatment has altered the concentration of defects or merely changed the fraction of defects which have become color centers by charge trapping. In an annealing experiment a given heat treatment may reduce the defect concentration and cause some of the remaining defects to lose their electronic charge. The actual defect concentration may be determined by re-irradiating with purely ionizing radiation until all of the uncolored defects have been converted to color centers, i.e., by re-establishing saturation coloring.

Determination of Defect Concentrations by Color Center Measurements.

From color center vs. dose data, a large amount of information can be obtained on the concentration of defects in crystals and on the rate defects are

introduced by radiation fields. Idealized color centers vs. dose curves for six simple, but different, situations are shown in Fig. 2. All of these have been observed experimentally. In the most simple situation a fixed number of defects which existed in the crystal prior to irradiation are converted to color centers. This is shown in Fig. 2(a). The experimental color center concentration vs. dose can usually be approximated by a saturating exponential. If after saturation coloring is attained, additional defects are introduced and then the coloring resumed, the curve shown in Fig. 2(b) will be obtained. Specifically, one could observe this behavior with a crystal that contained a fixed number of vacancies before it was exposed to an irradiation and a curve like Fig. 2(a) would be obtained. When saturation was definitely observed, the crystal could be exposed in a reactor and an additional number of stable vacancies formed by fast neutron bombardment. When the gamma-ray irradiations are resumed, the color center concentration would reach saturation at a higher level, e.g., as in Fig. 2(b). The number of defects introduced by the reactor bombardment would be the difference between the two saturation values.

Next consider a case in which the ionizing radiation field will create defects at a certain rate. If the sample contains a number of these same defects before irradiations are started, the color center vs. dose curve will be something like that shown in Fig. 2(c). The color center curve will actually lag behind the defect concentration curve but if defects are introduced at a relatively slow rate this lag will be very small. The equilibrium situation, if it can be called that, will be reached when the color center curve is increasing uniformly with time.

Fig. 2(d) is the case most likely to be encountered in a radiation damage experiment. There will be some defects present before irradiations are started, and the initial gamma-ray coloring will produce a small,

gradual increase in defects. When the initial coloring has reached the point where it increases steadily an exposure to reactor radiations or some other efficient means of introducing defects, will cause the rapid increase in defect concentration shown in the figure. This will be reflected in a rapid increase in color centers when radiations with ionizing radiations are resumed. Ultimately the coloring will increase with the same slope as the initial curve. If after the coloring curve is increasing uniformly, the crystal is modified in a way that increases the rate of defect formation by the ionizing radiation, a curve like Fig. 2(e) would be obtained. It is entirely possible that the treatment used to introduce defects may affect the crystal to the extent that defects are formed by the action of the ionizing radiation at a greater rate than they were initially. This situation would give rise to the coloring curves shown in Fig. 2(f). Note that in this case extrapolation of the coloring curves to the vertical line through the point where defects were introduced, in order to determine the number of defects created, would introduce an error if the two slopes differ greatly.

The data from a recently completed experiment appears to fit Fig. 2(f) very well.⁷ The object of this experiment was to determine the number of negative ion vacancies introduced into NaCl by plastic strain. Crystals of this material were first exposed to gamma rays until the F-center coloring reached saturation. They were then strained by plastic compression and when the gamma-ray irradiations were resumed there was a "jump" in the F-center concentration and the slope of the coloring curve increased. This can be explained as follows. The initial curve represented the coloring of vacancies that existed prior to irradiation and a gradual increase in F-centers due to the coloring of vacancies that "evaporate" from the original dislocations, plus those formed by one or a combination of the mechanisms described above. When the crystal was strained, vacancies were created and additional

dislocations were formed. When the gamma-ray coloring was resumed, the new vacancies were colored and the increased number of dislocations made possible an increase in the rate of vacancy evaporation. This technique can be utilized to provide information about the three mechanisms, described above, to account for the introduction of defects by purely ionizing radiations. The slope of the flat portion of the initial radiation curve could arise from contributions from all three mechanisms. In particular it represents an upper bound on the contributions from all of them. There are no compelling reasons to believe that the introduction of additional defects by strain or reactor irradiation should cause the Varley mechanism to be more effective. However, additional positive ion vacancies which are essential to the Crawford Nelson mechanism, can be introduced in this way. The dependence of the slope on the number of dislocations was described above. If it could be established that additional positive ion vacancies were introduced without changing the slope, Fig. 2(d), one could conclude that the Crawford Nelson model must produce less vacancies per unit dose than that given by the slope of the initial gamma-ray irradiation.

So far, it has always been assumed that there were some defects present before any irradiations were started. Certain types of defects may not exist prior to irradiation, i.e., it is possible to conceive of defects that can be formed only by radiation. In the simplest case, the curve of color centers vs. dose must start at zero and increase gradually with dose until a limiting fixed slope is reached. This case and similar but more complicated ones are discussed elsewhere.⁶

Measurements of Radiation Induced Defects by Color Centers

The background information required for an understanding of how color centers can be utilized to measure the defects introduced in crystals by various radiations was described in the preceding sections. The application

of this technique to three different crystals is described below. In these examples we will emphasize features in the measurements which illustrate the general aspects of the color center technique. For brevity, only minimum descriptions of the underlying color center research will be given. Thus some information which gives the appearance of being well established may ultimately require revision.

Reactor Induced Defects in NaCl.

The properties of some of the color centers created by irradiating NaCl are well known. It is well established that the band at 4650 Å (2.66 eV), the F-band, is due to a color center in which an electron is trapped by a single negative ion vacancy. Also, there is a band at 7200 Å (1.72 eV), an M-center, and several other bands which have not been definitely assigned to particular defects. A typical set of data obtained when defects are introduced in this crystal by reactor irradiation is shown in Fig. 3, complete details are given elsewhere.⁸ Data for two crystals is included. When both crystals have been exposed to gamma-ray irradiations of 3.6×10^7 r one crystal was irradiated in the reactor for 30 minutes. This introduced some radioactivity in the crystal and seven days elapsed before it could be handled. The other crystal was measured everyday to monitor the stability of the coloring and measuring equipment. Then the gamma-ray irradiations of both crystals were resumed. The F-center curves which were obtained closely resemble Fig. 2(c) and 2(d). It is particularly noteworthy that the slope changes very slightly after the reactor irradiation. Since this slope is a measure of the production of vacancies by ionizing radiation, this data indicate that the reactor irradiation did not modify the formation rate. From this it can be concluded that the reactor irradiation did not increase the dislocation concentration. This figure also includes data for three other color centers that are probably formed by charges trapped on defects, i.e.,

these three color centers do not involve impurities. The concentration of all three color centers is increased by the reactor irradiation.

The number of single negative ion vacancies created by the reactor irradiation can be computed from the "jump" in the data using Smakula's formula. This amounts to 7×10^{16} vacancies/cm³. The number of other defects created, i.e., the defects corresponding to the other absorption bands, cannot be computed at the present time since their oscillator strengths are not known. These measurements indicate that the theories of Kinchin and Pease and Seitz and Koehler correctly predict the number of vacancies formed by reactor neutrons.⁸

Annealing of the Reactor Induced Color Centers in Al₂O₃.

Synthetic single crystal Al₂O₃ (sapphire or corundum) is an ideal material for radiation damage studies. When irradiated with gamma rays at room temperature very little coloring is observed - even with doses of 10^9 r - at least in the region 2000 Å (6.18 eV) to 10,000 Å (1.23 eV) which can be measured with our present spectrophotometer. This lack of coloring can be explained in two ways. Either any color centers formed are very unstable and disappear immediately, or what is the more likely possibility, there are few defects or impurities in this material that form color centers in this region. In contrast, when Al₂O₃ is irradiated in a reactor, prominent absorption bands are formed at 6.02, 5.35, 4.85 and 2.64 eV. Studies on the growth of these bands during irradiation and some of their annealing characteristics have already been published.^{9,10} However, the Al₂O₃ annealing data illustrates some of the points already discussed so well that it is included here. Fig. 4 is a compendium of all of the annealing data for one crystal. First, this crystal was irradiated in the reactor until the three most prominent bands had reached a convenient height. Then it was irradiated with gamma rays to insure that saturation coloring had been achieved. Decay measurements that extended over twenty days indicate that this coloring is almost completely

stable. To determine the fraction of reactor-induced defects that remain after each anneal the following procedure is used:

- a) The crystal is heated at a specified temperature, usually in a wax or liquid metal bath, for a fixed time. From subsidiary measurements it was determined that an anneal of 20 minutes, at any temperature, caused the optical density to be reduced as much as anneals of several hours. Crystals are protected from interacting with the bath by suitable encapsulation.
- b) After each heat treatment crystals were subjected to a sufficient number of gamma-ray exposures to insure that equilibrium coloring was achieved. In Al_2O_3 this usually required a total dose of approximately 300,000 r which can be readily obtained.
- c) The entire procedure is repeated at each of a regular increasing series of temperatures.

The curves obtained for the 6.02 ev band, especially around 280°C , closely resemble Fig. 2(b), except that after each anneal the color center level is lowered. This is exactly what is expected since the annealing will remove defects. Overall, as the annealing temperature is raised the number of reactor-induced defects decrease and at 700 and 730°C they have entirely disappeared. Reactor irradiated samples which have been fully annealed do not color any more than virgin ones even with gamma-ray doses of 10^9 r.

This Al_2O_3 example also illustrates one of the complications which can arise. Following each anneal around 400°C the intensity of the 5.35 and 4.85 ev color centers increases instead of decreases. And in addition, when the gamma-ray irradiations are resumed these decrease with dose. Thus, saturation coloring of these bands was not achieved. One explanation for this involves

the equilibrium charge distribution obtained under gamma-ray irradiation at room temperature. Most likely these centers are shallow hole or electron traps which are partially emptied, and remain partially empty, under gamma-ray irradiation. This gives emphasis to a point included before. Namely, reliable determinations of defect concentrations can be made using this technique only when all or a known fraction of the defects have been converted to color centers.

Annealing of Reactor-Induced Color Centers in Fused Silica.

Very pure fused silica, such as Corning 7940 is colored only very slightly when exposed to gamma rays. However, similarly to Al_2O_3 reactor irradiations produce prominent absorption bands. In silica the peaks occur at 5.85, 5.48, 5.00, and 4.49 ev. If after the silica sample is removed from the reactor it is irradiated with purely ionizing radiation the bands increase, usually between 5 and 10 percent. This signifies that some of the reactor-induced defects had not trapped charges when the reactor irradiation was stopped. The annealing of these defects has been studied by the technique described in the previous section.¹¹ There is one difference, Al_2O_3 can be completely colored by relatively small doses, but in very pure fused silica doses of approximately 5×10^7 r are necessary to reach saturation. Because such irradiations are time consuming it is impractical to make complete annealing and recoloring measurements at many points. Thus, the recoloring step was omitted except at selected temperatures. The results of measurements on one sample are given in Fig. 5. Also, a typical set of recoloring curves are shown in Fig. 6. These are for the same sample after it had been annealed at 370°C and they most closely resemble Fig. 2(b). However, there is a slight indication that all of these curves are rising very slowly with dose. This would occur if the gamma-ray irradiations are

creating defects. This could be confirmed by extending the measurements to considerably higher doses. A slightly rising curve is comparable with Fig. 2(d).

In determining the defect concentrations shown in Fig. 5 it was assumed that in all of the coloring curves saturation was achieved. If all of the defects were not converted to color centers, i.e., if the curves do not represent saturation, the actual defect concentrations are higher than shown. Obviously, there are many uncolored defects after each anneal. After annealing at 540°C the optical absorption is barely detectable but one-third of the reactor induced defects remain. After the 600°C anneal the absorption has completely disappeared but one-fourth of the defects are still present. All of the defects detectable by color centers are not removed until the samples are heated to 700°C or slightly higher. When all defects have been removed the fused silica responds to further irradiation like virgin material, i.e., it colors very slightly when exposed to purely ionizing radiations and the same four prominent bands are induced by reactor irradiations.

Future Experiments.

The three examples described above on the use of color centers in radiation damage experiments were chosen to illustrate two points. First, they provide some insight into the basic physics involved and, somewhat superficially, some of the difficulties that occur. Secondly, they demonstrate the applicability of the color center technique by providing answers to some interesting physical problems. For example, it is found that the number of defects introduced in NaCl is in agreement with the current theories, and that, both Al_2O_3 and fused silica must be heated to 700 or 750°C to remove the (optically) observed reactor-induced defects.

There are many other radiation damage problems susceptible to the same methods. The number of vacancies induced in NaCl could be determined as a

function of the energy of the incident neutrons. The relation between crystal temperature and defect formation could be determined simply by doing irradiations at different temperatures. These are just two examples. In general it would appear that almost any radiation damage phenomena which involves defects that can be converted into color centers can be studied by the techniques described in this paper, or by very similar ones.

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Captions for Figures

- Fig. 1 Schematic representation of defects and color centers in alkali halide crystals..
- Fig. 2 Idealized color center vs. dose curves for a variety of defects vs. dose curves..
- Fig. 3 Defects induced in NaCl by reactor irradiation. Color center vs. dose curves for two crystals, are shown. After both crystals had been colored by gamma rays, one was reactor irradiated for 30 minutes. Then the gamma-ray irradiations were resumed. The "jumps" are proportional to the number of defects induced during the reactor irradiation.
- Fig. 4 Annealing of the reactor induced defects in Al_2O_3 . After each anneal the crystal is exposed to gamma rays until the coloring reaches equilibrium.
- Fig. 5 Annealing of the reactor induced defects in fused silica.
- Fig. 6 Recoloring of the reactor-induced defects in fused silica after the sample had been annealed at $370^{\circ}C$.

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

(a)

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+		+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

(b)

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	e	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

(c)

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+		+	-
-	+		+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

(d)

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	e	+	-
-	+	e	+	-	+
+	-	+	+	+	-
-	+	-	+	-	+

(e)

+	-	+	-	+	-
-	+	-	+	-	+
+	-	h	-	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

(f)

-	+	-	+	-	+	-	+	-
+	-	+	-	+		+	-	+
-	+	-	+		e	-	+	-
+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	-
+	-	h	-	+	-	h	-	+
-	h	-	+	-		-	+	-
+	-	+	-	+	-	+	-	+
-	+	-	+	-	+		h	+
+	-	+	-	+	-	+		+
-	+	-	+	-	+	-	+	-

(g)

FIGURE 1

DEFECT AND COLOR CENTER CONCENTRATION, USUALLY IN UNITS OF $10^{16}/\text{cm}^3$

— DEFECT CONCENTRATION
- - - COLOR CENTER CONCENTRATION

DOSE OF IONIZING RADIATIONS, USUALLY IN ROENTGENS

FIGURE 2

FIGURE 3

FIGURE 4

ANNEALING OF REACTOR INDUCED DEFECTS IN FUSE SILICA

RECOLORING AFTER ANNEALING REACTOR IRRADIATED FUSED
SILICA TO 370 °C

FIGURE 6