EFFECTS OF GAMMA IRRADIATION ON CERTAIN HALIDES

by

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INTRODUCTION

An important aspect of nuclear science is knowledge of the effects of high-energy radiation on materials. This is not a new topic. Investigators have long been concerned with the interaction of radiation and materials. However, the early interest was in the effects that occur to a radiation beam when the radiation interacts with matter. Some of these effects include scattering, range attenuation and diffraction phenomena.

It should also be noted that use of radiation was made in developing the theory of crystalline structure. In particular, X-ray diffraction was fundamental in the development of crystal structure theory. Knowledge of radiation and knowledge of the solid state of matter have had a closely related development.

The discovery of nuclear fission and the development of a nuclear chain reactor in the 1940's brought to light the importance of radiation effects on materials. A reactor presented the first instance of materials being subjected to a high level radiation environment over a long period of time.

It became necessary to know what would happen to a material when it was used in a nuclear reactor. Radiation damage would influence many of the material's useful properties. Knowledge of the effects of radiation on various materials was needed for selection of suitable reactor materials. Consequently a new field of research was required to provide the answers. A knowledge of radiation effects had to be based on actual investigation of materials exposed to a radiation environment.

As has been pointed out (1, p. 3), there is a close correlation

between solid state physics and the field of radiation effects. The solid
state physicist is concerned with the nature of crystalline structure and
its imperfections. The engineer wants to know what type of radiation
damage occurs in a material, what are its causes and what limitations
will this impose on the use of the material.

For an understanding of the phenomena of radiation effects it is
important to have a material with a simple structure. With such a material
it is possible to explain radiation effects on the basis of a simple, yet
well established structure. Alkali halide crystals have a face-centered
cubic structure which should meet this requirement. Alkali halides have
been used extensively in the study of radiation effects. The alkali
halides have also been used extensively for research in solid state
physics. As a result, choice of alkali halide crystals as a material for
study of radiation damage seems suitable.

Radiation damage occurs on a microscopic scale. However, the evalua-
tion of radiation damage must result from observation of macroscopic
property changes occurring in a material. An explanation of the damage
depends on a theoretical discussion of the property changes. Various
properties of crystals can be selected for study. These include electrical
conductivity, thermal conductivity, optical absorption, density changes,
changes in elastic properties, electron spin resonance, diffraction
effects, etc. Whatever property is chosen for study, the experimental
results should verify a plausible theoretical model.

At the microscopic level the interaction of photons with a material
results primarily in ionization. Charged particles interact with solids

in a manner to give both ionization and displacements, i.e. lattice atoms removed from their lattice sites. Neutral particles, such as neutrons, collide directly with the nuclei of lattice atoms to produce displacements. A secondary effect of neutral particle interactions is ionization and additional displacements. Displaced atoms from the first collision, which have been ionized, interact with other lattice atoms to give the resulting ionization and displacements. The macroscopic property changes which can be observed are explained on the basis of the interaction mechanisms which have just been mentioned.

In radiation effect studies, changes in observable properties due to irradiation of the material are noted. The results are then used as a verification of a particular existing interaction model or serve as the stimulus for advancing a new model.

THEORETICAL DISCUSSION

Structure of Alkali Halide Crystals

In a solid the distinguishing characteristic is the order exhibited by its constituents. This order is maintained by the forces existing between atoms comprising the solid. The ionic crystals are assumed to consist of positive and negative ions, with a binding energy between them to maintain the order. The positive and negative ions are considered as charged particles. Born was the first to develop a theory to account for the structure of ionic crystals. His theory is treated in Dekker (2) and reviewed in Mott and Gurney (3).

The arrangement of the ions in an ionic crystal is such that the Coulomb attraction is stronger than the Coulomb repulsion. The ionic bond between the ions is a balance of the electrostatic attractive interaction of oppositely charged ions and the repulsive interaction of ions of the same charge. The degree of ionization of the constituent ions in an ionic crystal is such that the electronic configuration of all ions corresponds to closed shells. For example, for LiF, the electron configurations of the neutral atoms are:

Li $\quad$: $\quad 1s^2 \, 2s$

F $\quad$: $\quad 1s^2 \, 2s^2 \, 2p^5$
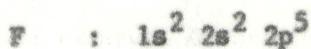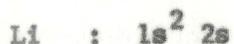
This contrasts with singly charged ions which have electron configurations of:

Li$^+$: $\quad 1s^2$

F$^-$: $\quad 1s^2 \, 2s^2 \, 2p^6$

The latter configuration is the same as for helium and neon, respectively. The inert gas atoms have closed shells and a spherically symmetric charge distribution. It is expected that the charge distribution on each ion in the ionic crystal then has approximately spherical symmetry. There may be some distortion near the region of contact with neighboring ions (4).

If the charge distribution is spherically symmetric, then the forces between ions depend only on the distance between the ions. It is found that the lattice energy of ionic crystals depends on the attractive forces and short range repulsive forces. The latter are due to the tendency of ions to resist the overlapping of electron shells. The lattice energy is defined as the energy required to move an ion to an infinite distance from its lattice site. The ion binding energy is the resultant of the attractive and repulsive forces and the minimum energy occurs at the equilibrium position of adjacent ions. This distance determines the lattice constant. The lattice constant is the separation distance of nearest neighbor ions in the crystal and is a constant value for each type of ionic crystal.

An expression for the lattice energy has been given as:

$$E_L = -N \, \alpha \frac{e^2}{a_o} \, (1 - \frac{1}{n})$$

where N is the number of ion pairs; α is the Madelung constant; a_o is the lattice constant and n is a repulsive exponent (2).

A development of the lattice energy for an alkali halide has been given by Kittel (4). Let ϕ_{ij} be the interaction energy between ions i and j. The total energy between one ion, i, and all other ions is

$$\phi_i = \sum_j{}' \phi_{ij}$$

where $\sum_j{}'$ indicates that the summation includes all ions except j=i. The interaction energy has the form

$$\phi_{ij} = \frac{\lambda}{r_{ij}{}^n} \pm \frac{e^2}{r_{ij}}$$

where + is used for like charges and - for unlike charges. λ is a constant and r_{ij} is the distance between ions i and j. The repulsive potential is $\lambda/r_{ij}{}^n$ and the Coulomb potential energy is $\pm \frac{e^2}{r_{ij}}$.

Let U_o be the total lattice energy of a crystal with 2N ions. Then $U_o = N\phi$. The total lattice energy is the energy required to separate the crystal into individual ions an infinite distance apart. Further, let $r_{ij} = p_{ij} R$ where R is the distance between nearest neighbors in the crystal, and p_{ij} is a dimensionless quantity. Then

$$\phi_{ij} = \frac{1}{p_{ij}{}^n} \frac{\lambda}{R^n} \pm \frac{1}{p_{ij}} \frac{e^2}{R}$$

$$\text{or} \quad \phi = \frac{\lambda A_n}{R^n} \pm \frac{\alpha e^2}{R}$$

where $A_n = \sum_j{}' p_{ij}{}^{-n}$ and $\alpha = \sum_j{}' (\pm) p_{ij}{}^{-1}$.
α is the Madelung constant and has a particular value for each type of crystal. At the equilibrium separation, R_o, $\partial\phi/\partial R = 0$, so

$$- \frac{n\lambda A_n}{R_o{}^{n+1}} + \frac{\alpha e^2}{R_o{}^2} = 0 .$$

It follows that $\phi = - \dfrac{\alpha e^2}{R_o} (1 - \dfrac{1}{n})$. With this value for ϕ, $U_o =$

$- \dfrac{N\alpha e^2}{R_o} (1 - \dfrac{1}{n})$ where $n \sim 10$. This is the total lattice energy.

The Madelung constant can be determined in the following way. With

$$\alpha = \sum_j{}' (\pm) p_{ij}^{-1}, \quad \text{then} \quad \frac{\alpha}{R_o} = \sum_j{}' (\pm) \frac{1}{r_{ij}}$$

where r_{ij} is the distance of the j-th ion from a reference ion, i. R_o is

the spacing between ions. For a one dimensional case

$$\frac{\alpha}{R_o} = 2 \left[\frac{1}{R_o} - \frac{1}{2R_o} + \frac{1}{3R_o} - \frac{1}{4R_o} + \text{----} \right]$$

Therefore, $\alpha = 2 [1 - 1/2 + 1/3 - 1/4 + \text{----}]$.

The 2 enters the equation from the fact that ions lie to the left and to

the right of the reference ion. Since $\ln(1+x) = x - \dfrac{x^2}{2} + \dfrac{x^3}{3} - \dfrac{x^4}{4} + \text{----}$

it follows that $\alpha = 2 \ln 2$ for a one dimensional case. When the three

dimensional case is considered, it is difficult to get a series convergence

to find an adequate value for α. Improvement may be gained by treating a

three dimensional neutral group of ions. The potential of a neutral

assembly falls off faster as the distance from the reference ion of the

assembly increases.

The repulsive exponent is given by the expression

$$n = 1 + \frac{18 \, R_o^4}{K e^2 \alpha}$$

where R_o is the equilibrium separation of ions and K is the compressibil-

ity. If K is 3.3×10^{-12} $cm^2/dyne$ then n is 9.4 for NaCl.

Refinements to the classical Born theory result from consideration of van der Waal forces and from a quantum mechanical analysis of the problem.

It should be noted that the crystal structure is not in a static condition. There will be lattice vibrations of the ions about their equilibrium positions. The lattice vibration is a thermal phenomena and hence is a function of the temperature of the crystal.

Defects in Alkali Halide Crystals

Much of the elementary theory of the crystal structure is based on the notion of a "perfect crystal". Such a crystal has all lattice positions of the crystal occupied by ions or atoms. In nature, however, perfect crystals do not occur and some discussion must be given to defects in the crystal structure.

The presence of defects involves a consideration of the thermodynamics of a solid (2, 3). The most common types of defects are vacancies and interstitials. Schottky defects are pairs of vacancies. For ionic crystals these are unoccupied positive and negative ion sites, paired to preserve charge neutrality. Frenkel defects are interstitial ions or ions displaced from the normal lattice position. For an ionic crystal, the Frenkel defect is an interstitial ion paired with a vacant lattice site to maintain the charge neutrality. It can be shown that the number of positive ion vacancies must be of the order of magnitude of the negative ion vacancies. This is based on a consideration of space charge effects.

There is an activation energy associated with the formation of ion vacancies. The determination of the energy involves a consideration of the thermodynamics of the solid. Dekker gives a discussion of some of the factors involved (2). The energy of formation of Schottky defects is about the same as the energy of formation of Frenkel defects. The activation energy is based on the Born lattice theory. However, it is also necessary to evaluate the effect of polarization on the rest of the lattice when an ion is removed. An expression for the activation energy is (2)

$$A = \frac{\alpha e^2}{a_o} \left(1 - \frac{1}{n}\right) - \frac{1}{2} e^2 \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{R_+} + \frac{1}{R_-}\right)$$

where α is the Madelung constant; a_o is the lattice constant; e is the electronic charge; n is the number of vacancies; ϵ is the dielectric constant and R_+ and R_- are radii of the Jost charge model.

The existence of vacancies is used to explain the process of self-diffusion in a crystal. Also, the conductivity of a crystal is associated with the motion of vacancies. For most ionic crystals the motion of positive ion vacancies accounts for the conductivity of the crystal.

A further type of defect is the impurity atom. This may be an impurity atom occupying either a lattice site or an interstitial position. Normally, an impurity atom is added by diffusion or occurs through trans-mutation. Transmutation may result from a nuclear reaction, as from neutrons interacting with one of the lattice atoms.

The defects discussed above are simple defects which may be considered as point defects. Composite defects can also occur and are an aggregation

of point defects. In many alkali halide crystals the defects tend to cluster forming localized regions of defects.

A second type of defect is the line defect or dislocation. A dislocation may be described as a distortion of the arrangement of a crystal lattice. For alkali halide crystals, a simple edge dislocation would be the introduction of a plane of positive and negative ions in the lattice. Charge neutrality must be maintained within this extra plane, however. The lattice structure is disturbed near the edge of the extra plane which forms the dislocation line. A similar type of dislocation line is associated with a screw dislocation.

Several features of the line defects can be cited (1, p. 67). The line defect follows a closed path in the crystal or extends to the surface. Motion of the line defect causes deformation of the crystal. The motion of the line defect is restricted, which differs from the motion of point defects. It is possible that dislocations may also occur by clustering of vacancies.

The presence of both point and line defects is used to account for the alterations in the properties of a material.

Interaction of Radiation with Alkali Halide Crystals

The interaction of radiation with the atoms or ions of a solid involves the transfer of energy from the moving particles of the radiation beam to the lattice atoms of the solid. The method of energy transfer varies with the type of radiation. The method of transfer of energy will, in turn, determine the damage that results to a given solid.

A short discussion of the interaction mechanisms for different types of radiations will be presented.

Charged particle interactions

Two kinds of collisions can occur with charged particles. Both types will slow down the moving charged particle. In elastic collisions, momentum and energy are conserved. In inelastic collisions, some of the energy is used in excitation or ionization of the electrons of the lattice atoms.

When the charged particles have high energy, the charged particles are slowed down by the energy loss resulting in ionization or excitation of the target atoms. As the charged particles are slowed down, an energy is reached where a change in the predominant method of energy loss occurs. Below this transition energy, energy loss occurs primarily by elastic collisions rather than by ionization. The transition energy is usually designated E_i. For alkali halides a value of the transition energy is given by Seitz (5) as $E_i = \frac{1}{8} \frac{M_1}{mI}$ where M_1 is the mass of the charged particle, m is the mass of the electron and I is the first electron excitation energy level of the lattice atom. When the kinetic energy of the moving charged particle drops below E_i it is assumed that energy loss is due only to elastic collisions.

The specific rate of energy loss is also of interest here. The specific rate of energy loss is the amount of energy loss per unit path length traveled by the moving particle in the solid. For energy loss by ionization a suggested value (6) is

$$-\frac{dE}{dx} = \frac{4\pi e^4 Z_1'^2}{mv^2} N_o Z_2'^2 \ln \left[\frac{2 mv^2}{J}\right]$$

where v = velocity of moving particle

$Z_1' e$ = charge of moving particle

N_0 = density of atoms in material

Z_2' = effective number of electrons in material to be excited

J = mean excitation potential of electrons in stopping material

The theory required to develop an expression for energy loss rate is complicated so the above expression is at best an approximation. Evans (7) has a complete development of this subject.

It is also necessary to include a consideration of defect production by a displacement of ions from lattice sites. When there is charged particle bombardment, the displacement process occurs. Elastic collisions produce a cascade of further displacements.

The type of model chosen to explain the interaction of charged particles and the crystal depends on the distance of approach of the charged particle to the atom in the crystal.

Rutherford collisions occur when the charged particle penetrates close to the nucleus of the target atom. The laws of classical Rutherford scattering can be used to explain this interaction. When the charged particle approaches close to the electron cloud surrounding the nucleus the repulsive force between the two nuclei is reduced due to the screening of the clouds of electrons. According to Bohr (8), it is reasonable to assume that, in general, the screened Coulomb potential energy is of the form $V(r) = \dfrac{Z_1 Z_2 e^2}{r} e^{-r/a}$. Here, Z_1 is the atomic number of the moving particle; Z_2 is the atomic number of the target atom; r is the distance between charged particle and the target atom; e is the

electronic charge and a is a parameter called the screening constant.

If the charged particle does not penetrate close to the atom, i.e. r >> a, the interaction may be considered as that of two hard spheres. Thus, a treatment of the interaction can be made in terms of the mechanics of "billiard ball" elastic collisions.

The importance of these models becomes clear when we are considering the cross section for energy transfer. In Rutherford scattering there is a preference for small values of energy transfer. In the hard sphere model there is equal probability for all values of energy transfer to the target atom. Values of energy transfer ranging from zero energy to a maximum value of energy transfer are equally probable.

The number of displacements in a material can be theoretically estimated, based on a cascade process in which lattice atoms displaced by the moving charged particle will strike other lattice atoms and displace them, provided sufficient energy is transferred to the struck atoms.

It can be seen that in charged particle irradiations, displacement of ions is possible. Thus both ionization and displacements resulting from elastic collisions will produce defects in the alkali halides.

It is very difficult to calculate the exact number of displaced atoms. The displacement process is a cascade one, in that atoms displaced by the moving charged particle will displace other lattice atoms if they have sufficient energy transferred to them. Thus a primary struck atom may produce a number of subsequent displacements. The computation of the total number of atoms displaced will depend on whether a Rutherford or hard sphere model is assumed for the energy transfer process.

Neutron interactions

Fast neutrons interact only by direct collision with the nuclei of lattice atoms since they carry no charge. In the case of neutron irradiation, energy loss occurs by elastic collisions. However, there is a possibility that the displaced atoms may be ionized. The displaced lattice atoms will acquire an energy which depends on the angle of deflection. If one assumes isotropic scattering, there is an equal probability for values of energy transfer from zero to the maximum energy transfer. However, there is a certain anisotropy in the angular deflection of the scattered neutrons. This should be taken into account when calculating the mean energy transferred by fast neutrons. The anisotropic correction factor has a value varying usually from 1/2 to 2/3.

Gamma ray interactions

The interaction of gamma rays with matter results in the photoelectric effect, Compton scattering or pair production. The energy or energy range of the gamma rays determines which process will predominate. As a result of gamma ray interaction with atoms of some solid, the ejection of electrons with an energy close to that of the incident gamma ray may take place. These electrons will further interact with other lattice atoms of the solid and lose energy, mostly by ionization. As mentioned before, ionization is an important effect in ionic crystals. When the energy of the internal electrons is very high there is a very small probability that lattice atoms may be displaced by elastic collisions. The method for calculating the cross section for Compton interactions and the number of lattice atoms displaced is developed in Dienes and

Vineyard (6).

Several new mechanisms for displacement of lattice atoms by photons have been suggested. One of these mechanisms has been advanced by Seitz to explain the formation of color centers in alkali halide crystals. Another model has been proposed by Varley and is based on a multiple ionization process. These ideas will be discussed in detail later.

Defects and the Physical Properties of Alkali Halides

As stated before, radiation damage occurs at the microscopic level. However, to observe the effects of radiation damage it is necessary to measure macroscopic properties. Thus it is important to select properties that can both be easily measured and are subject to appreciable change under the influence of radiation.

One of these properties is conductivity. In alkali halides the conduction of charge is by the motion of positive ion vacancies. Thus any change in the motion of positive vacancies will show up as a change in the conductivity or resistivity. It is found that exposing crystals to particle and photon radiation will cause a change in conductivity. This makes conductivity or resistivity measurements very useful for study of the influence of defects in alkali halides.

A second property easily affected by irradiation is the change in optical density of alkali halides. Alkali halide crystals color easily when exposed to radiation. Measurement of the change in optical density resulting from exposure to radiation is an effective means of determining

the amount of radiation damage. The different types of color centers formed in alkali halide crystals give some indication of the nature of the defects produced in these crystals. The formation of vacancies and interstitials is evidenced by the trapping of electrons by defects to form color centers.

A third property influenced by radiation is change in density of the crystals. Some of the alkali halide materials will alter their density when exposed to the different types of radiation. This change in density is usually determined by gravity measurements or by a change in X-ray diffraction patterns. Some idea of the defects causing the change in density can be obtained from a study of density changes resulting from irradiation and the recovery of the lattice following the irradiation.

Mechanical properties are also studied to determine what effects imperfections have on alkali halides. Generally, measurement of many of the mechanical properties of alkali halide crystals is difficult. Thus mechanical property studies do not yield much useful information, as is true for metals. Several investigators have attempted to find a change in the hardness of alkali halide crystals following irradiation.

The formation of color centers is probably the most widely studied property. However, in order to explain the mechanism of radiation damage in alkali halides, intensive and extensive study of the effects produced in different properties by irradiation is necessary.

REVIEW OF LITERATURE

There have been several models proposed as an explanation for the creation of defects in alkali halide crystals by photons. One model is proposed by Seitz (9) and reviewed by Markham (10). According to Seitz's model, vacant lattice sites are generated at a dislocation line in the crystal. Excitons or localized regions of electronic excitation consisting of a bound hole-electron pair in an excited state, are generated in the solid during the irradiation. These are responsible for creating high temperatures. The excitons can travel through the solid but will interact at lattice vacancies or other imperfections transferring their energy into lattice vibrations of the adjacent atoms producing a localized region of high temperature. Most frequently the position of the interaction is located at points along an edge dislocation. The edge dislocation results from extra planes of atoms in the lattice structure. The points of inter-action are referred to as jogs. Jogs occur when the dislocation line drops down one layer of atoms. Near jogs, the bonding of the lattice atoms is weakened. The energy transferred to the lattice due to the interaction is sufficient to displace a regular lattice atom into the extra plane of atoms. Hence an extra vacancy is created and will diffuse away from the dislocation. As the atoms fall into the extra plane of atoms the disloca-tion line appears to move or "climb".

Seitz (9) suggests that there are about 10^{15} atoms/cm^3 adjacent to dislocation lines. Thus, an edge dislocation must climb through 1000 atomic distances to generate 10^8 vacancies/cm^3, an appropriate order of magnitude.

Free electrons and holes result from irradiation in crystals. Since
the binding energy of an electron to an anion vacancy, which is an F-
center, is higher than that of a hole-electron pair in an exciton, there
is a large probability for F-center formation according to this model.

Varley has proposed a different model to explain the coloring of
alkali halide crystals (11, 12, 13). The failure of elastic collision
theory to explain coloration in crystals with electron bombardment caused
him to think of a better explanation. Varley's model is based on multiple
ionization of negative halogen ions by photons. The multiple ionization
is to be accompanied by movement of the stripped electrons away from the
lattice site. The multiple ionized halogen will then find itself with a
positive charge and the electrostatic repulsion of its neighbors will tend
to dislodge it to an interstitial position. It is proposed that the
dislodging process occurs in a time interval very short compared with
the recombination time of the electrons to the halogen ion. Later, the
interstitial halogen ion may recover all but one of its electrons and
remain neutral. If lattice vibrations do not move the neutral intersti-
tials back to the original site, the vacancy will trap an electron and
form an F-center.

The requirements for such a process are that;
1) there is strong ionic bonding in the crystal,
2) the recombination time of the multiple ionized halogen ion and its
   electrons is sufficiently long,
3) there is a sufficiently large cross section for multiple ionization.

Varley suggests cross section values of 10^{-16} cm^2 for single ionization and 10^{-17} cm^2 for double ionization.

With this mechanism, the expression for the number of interstitial atoms formed per cm^3, n, is given by

$$n = N_o \, F \, t \, \sigma$$

where N_o is the number of ions/cm^3, F t is the flux time and σ is the cross section. If $\sigma \sim 10^{-19}$ cm^2, the number of displacements per unit flux time is about 10^3 displacements per cm^3.

Howard and Smoluchowski (14) considered some of the aspects of the Varley mechanism. These aspects are:

1) average lifetime of the doubly ionized center against the recapture of electrons,

2) ease with which the positive halogen ion can reach an interstitial position,

3) the stability of an interstitial against return to its original site.

They conclude that the doubly ionized halogen ion requires a lifetime of a magnitude equal to that of the period of a lattice vibration (10^{-12} sec.) to avoid electron recapture. It is possible that below a critical density of conduction electrons, the lifetime of a halogen center is sufficiently long to form an interstitial.

The lifetime of a center is the time for electrons to reach the center, plus the time, once the electron is in the vicinity of a center, for the electron to be captured.

The lifetime for the center is

$$\tau = \int_{0}^{\bar{r}} \frac{Kr^2}{2ue} \, dr = \frac{K}{8\pi e u n}$$

where K is the dielectric constant, u is the electron mobility, $\bar{r} = [(4/3\pi)n]^{-3}$, and n is the density of conduction electrons. For NaCl at 200°K, $\tau \approx 10^5/n$ sec. Then the density of conduction electrons, n, is 10^{17} per cm^3 and $\tau > 10^{-12}$ sec. The doubly ionized center should be able to escape to an interstitial position.

These authors refer to other papers to state that;
1) from potential considerations the positive halogen ion should get to an interstitial position,
2) the energy required for the interstitial to return to the interstitial site is too large for the return of an interstitial to occur often. Thus, interstitials should form readily.

Dexter (15) points out that the work of Howard and Smoluchowski is based on a "hard sphere" or "very tight binding" approximation, in which electrons are localized at a particular site. In an energy band picture, a double ionization corresponds to creating two positive holes around some halogen site, maybe in different filled bands. Since Coulomb repulsion is very strong here, the two holes would separate in different directions. Later, the crystal would have two separated holes or halogen atoms. The time for this to occur would be about 10^{-15} sec. Once the two holes separate there is no reason for a halogen ion or atom to be ejected to an interstitial position. Thus the Varley mechanism would not apply. After considering free particles and the case where both would lie in the inner shells (K or L) of the atom, this author concludes that the Varley

mechanism does not apply when outer holes are considered or when only inner holes are involved. However, Dexter feels that the multiple ionization process may be a strong possibility in certain cases.

Klick (16) has presented the idea that although the electrostatic repulsive forces are neutralized according to Dexter, the energy released by the transfer of an electron from a neighboring halide to the multiple ionized halogen can be utilized to produce an interstitial-vacancy defect pair. When the electron transfer occurs the electron exchange forces attract the two halogen atoms, thus forming a halogen molecule. Since the halogen molecule is small it will fit into the space normally taken by one of the halide ions. This then leaves a halide ion vacancy. When the vacancy is filled by an adjacent halide ion the halogen molecule and the vacancy are separated. When the vacancy and the molecule trap electrons, an F-center and an H-center are created.

Schulman and Compton (17) in reviewing the formation of color centers by ionization, state that thus far there have been no experiments devised which can distinguish between single or multiple ionization as the more likely mechanism for formation of color centers. Both processes are possible and the efficiency for formation is of reasonable magnitude in each case.

A number of techniques have been used by investigators to determine defect formation in alkali halides. One of the more effective ones is the study of color center formation. Alkali halide crystals readily color with radiation. Thus it is possible to study the effects by measuring color center density and changes in the color center density.

Mador et al. (18) carefully investigated the coloring of NaCl and LiF crystals with X-rays and subsequent bleaching of the centers. They made their optical measurements in a direction perpendicular to the direction with which the X-rays penetrated the crystal. They concluded for short exposures that the number of F-centers produced was proportional to the total radiation absorbed. They were able to determine that the vacancies created, resulting in color centers, were the result of X-rays. Their attempt to account for optical bleaching was to postulate (1) the transfer of F-center electrons to the conduction band, and (2) the trapping of conduction electrons by holes and vacancies.

Kobayashi (19) studied the annealing effects occurring in NaCl. Optical absorption was one of the techniques used. He used 350 Mev protons as the bombarding particles. Several different color centers were formed. He found when studying the annealing, that as the temperature is first raised the number of color centers present decreases slightly. However, as the temperature increases to a higher range the decrease in the number of color centers is quite rapid. At about 250°C. color centers disappear altogether.

Levio and Smoluchowski (20) studied color centers produced in KCl by proton irradiation. They first irradiated KCl with 400 Mev protons. Then they exposed the crystals to X-rays. The result was a deep coloration throughout the entire crystal. This was done because long irradiation by protons alone tended to bleach the crystals. The characteristic coloration of KCl was brought back by the X-ray exposure. The proton irradiated crystals were deeply colored as compared with the shallow coloring of

control crystals exposed only to X-rays. One explanation offered is that vacancies are produced throughout the entire crystal when irradiation is by protons. The photoelectrons produced by X-rays are then trapped at vacancies to form the color centers throughout the crystal.

Bron and Nowick (21) made a study of the fractional exposure effects on the F-center concentration in alkali halides. That is, they sought to determine if the fraction of cross-sectional area of a crystal exposed to X-rays would influence the concentration of F-centers. Their work indicated that the F-center concentration is independent of the fraction of the crystal exposed. This was in contradiction of some earlier studies by others.

Billington and Crawford (1) discuss several topics pertinent to optical absorption in alkali halides. Effects of high energy particle irradiation rarely differ from photon irradiation effects. One would expect different types of defects to result from particle irradiations than from photon irradiations. The authors point out much knowledge is needed to explain (1) the creation of point defects by photon interactions and (2) energy transfer processes. Use of more advanced experimental techniques may help explain why there appear to be no differences in effects from ionization producing radiation and displacement producing radiation.

Another fact these authors point out is that effects produced by displacements are difficult to separate from those that are due to ionization since they occur simultaneously. This is true in the case of neutron irradiation in a reactor because there is always a gamma flux present.

Qualitative differences in absorption bands produced by charged particle irradiation compared with photon produced absorption bands were cited by these authors from work they reviewed. In the case of particle irradiation certain absorption bands are more prominent and more stable than are bands from photon exposures.

RESEARCH PROBLEM

The determination of radiation effects or radiation damage is based on observation of property changes in a material. Alkali halides have a simple structure which makes them suitable for radiation effects studies. Color centers are readily formed in irradiated alkali halide crystals. The change in optical density resulting from the formation of color centers is an easily observed property change, well suited for radiation effects studies in alkali halides.

With these facts in mind, it was decided that this research project should consist of a qualitative and comparative study of the formation and annealing of color centers in several alkali halide crystals. The equipment needed for color center studies is not particularly complicated and the techniques required are not difficult. The large amount of information published on this subject can be helpful for work in this area.

The problem consisted of a study of the formation of color centers in irradiated alkali halide crystals. It is essential to know the type of color centers formed and the variation of intensity of these color centers with the dose of radiation received by the crystals. The process of annealing of irradiated crystals was studied to see what parameters or variables influence the annealing process.

It should be pointed out here that this comparative study of the effects of radiation on some halides was mainly exploratory in nature and only a part of a detailed study of this phenomena.

EXPERIMENTAL EQUIPMENT

The description of the materials under investigation, the equipment and radiation facility used, is given below.

Materials

Three kinds of alkali halide materials were studied. They were sodium chloride, potassium chloride and lithium fluoride. The samples used were obtained from the Harshaw Chemical Company. The approximate dimensions of the speciums are 25 x 12 x 5 mm, with a volume of about 1.36 cm^3.

Spectrophotometer

Measurements of optical density of the samples were made with a Beckman Model DU spectrophotometer. The spectrophotometer consists of a light source, monochromator to select light of a particular wavelength, cell holder and a phototube housing containing phototubes and amplifier circuit. The photocurrent produced by the phototube gives a measure of the light transmitted through the sample.

The principle of operation of the spectrophotometer is as follows (see Figure 1). Light from a light source is focused by a condensing mirror and directed as a beam to a diagonal slit entrance mirror. The entrance mirror deflects the light through the entrance slit and on to a collimating mirror in the monochromator. The light falling on the collimating mirror is rendered parallel and reflected to the quartz prism. The light undergoes refraction as it passes through the prism. The back
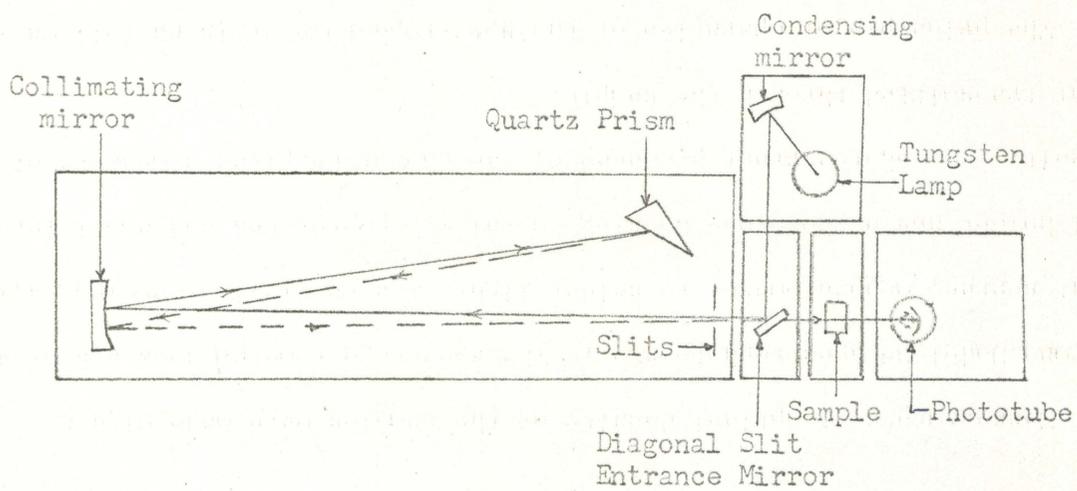
Figure 1. Diagram of spectrophotometer optical path.

surface of the prism is aluminized so that the light refracted when pass-
ing the first surface, is reflected back through the prism, undergoing
further refraction as it emerges from the prism.

The desired wavelength of light is selected by rotating the wavelength
selector which adjusts the position of the prism. The spectrum is
directed back to the collimating mirror which centers the chosen wavelength
on the exit slit and sample. Light passing through the sample strikes
the phototube producing a photocurrent. The photocurrent is amplified and
registered on a null meter (22).

Measurement of optical transmittance, or absorbance is made by
balancing the spectrophotometer circuit to give zero deflection on the
null meter when no sample is present. A sample is placed in the cell
compartment and the circuit is again nulled by varying a rheostat cali-
brated in units of transmittance or absorbance.

With the spectrophotometer, the absorbance of light passing through
a sample, i.e. the optical density of the sample, can be measured for
each particular wavelength chosen for study. As mentioned above, the
wavelength is selected by rotating a calibrated dial which is connected to
the prism mount and which rotates the prism.

A hydrogen lamp serves as the ultraviolet light source for the wave-
length range of 200 to 320 mu and a tungsten lamp provides light in the
visible range of 320 to 2000 mu.

Radiation Facility

The cobalt-60 radiation facility at the Veterinary Medical Research Institute was used as the gamma ray source for this experiment. The facility is loaded with about 8,500 curies of Co-60.

The cobalt capsules are cylindrical in shape, about 1.5 cm in diameter and 14 cm long, and are clad in stainless steel. The cobalt capsules are located below ground level (see Figure 2). Samples are thus lowered to and raised from the irradiation area. The capsules are arranged so that they circumscribe the irradiation area and the sample to be irradiated receives a uniform gamma dose.

The cobalt source capsules are arranged so that they can be positioned at varying distances from the sample. In order to do this the capsules are attached to an arm fixed to a pivot. The capsules are swung in toward the irradiation area and positioned at the necessary distance from the sample to give the desired radiation intensity.

A brass tube containing the sample is attached to a rack and pinion drive mechanism which lowers the sample into and raises it from the irradiation area.

To mount the crystal for this experiment the following arrangement was used (see Figure 3). A wire holder was fabricated, into which the sample crystals were clipped. The holder was arranged so the wire surrounds the edges of the crystal and does not obstruct the penetration of the radiation through the crystal. The holder had a wire extending up to a rubber stopper. The crystal mount was then inserted into a glass tube with the rubber stopper holding the mount firmly in place. The glass

Figure 2. Co-60 radiation facility.

Rubber
Stopper

Support
Wire

Glass
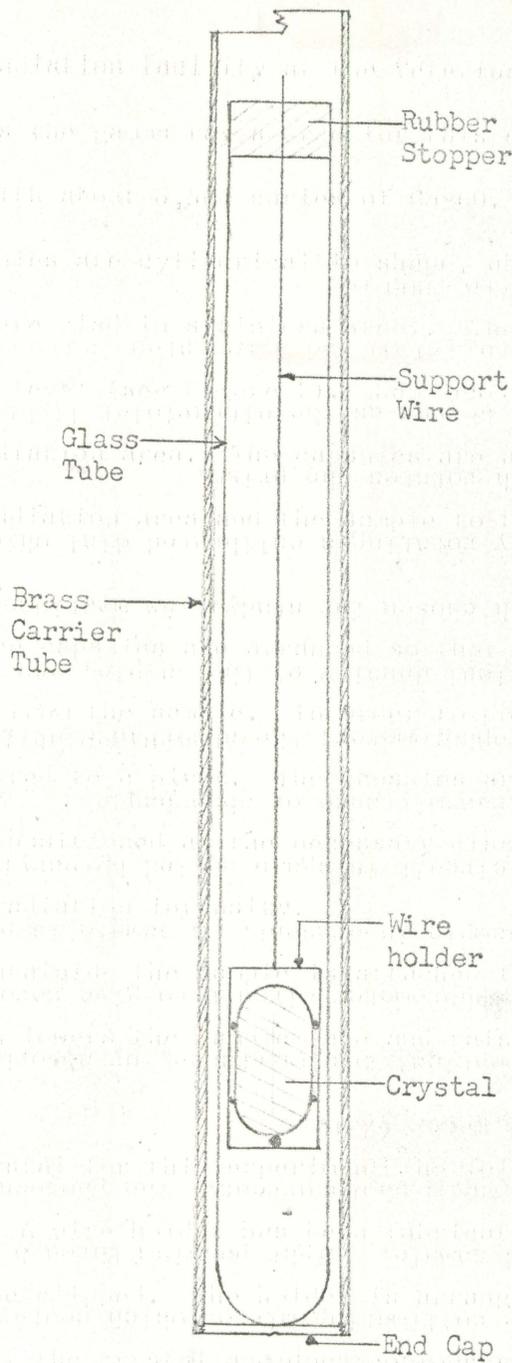Tube

Brass
Carrier
Tube

Wire
holder

Crystal

End Cap

Figure 3. Schematic diagram of crystal mounting arrangment.

tube with mount was then inserted into the brass carrier tube. Using this type of mounting the crystal samples were accurately repositioned for each exposure.

Dosimetry

The radiation intensity at the sample position was measured with a chemical dosimeter. A ferrous sulphate solution (Fricke solution) was used as the dosimeter. The principle of the ferrous sulphate dosimeter is based on the oxidation of ferrous ions (Fe^{++}) to ferric ions (Fe^{+++}) in an aqueous solution. Ionization produced by photon irradiation will dissociate H_2O molecules into free H and OH radicals in an aqueous solution. The free radicals formed will react with ferrous ions in several types of reactions with the result that ferrous ions are oxidized to ferric ions. The number of ferric ions produced depends on the radiation dose received.

The amount of ferric ions created can be determined by spectrophotometric analysis because the ferric ion strongly absorbs ultraviolet light of 304 mu wavelength. The optical density of an unirradiated sample and an irradiated sample are measured. The difference in the optical density is a measure of the number of ferric ions created. The difference in optical density is used in the calculation of the dose rate or total dose. Price (23) gives an equation for dose rate as

$$R \ (r/hr) = \frac{10^9}{6 \gamma t} (A_{sample} - A_{blank})$$

where A_{sample} and A_{blank} are optical density of irradiated and unirradi-

ated solutions, respectively; ϵ is molar extinction coefficient; Y is

ferrous sulphate yield; micromoles (uM) of ferric ions per liter per 1,000

r; b is sample thickness in cm; and t is irradiation time in hours.

EXPERIMENTAL PROCEDURE

First of all, the optical density of the crystals was studied as a function of wavelength of transmitted light. The optical density was measured for each wavelength studied, the wavelength spectrum extending from 200 mu to 1000 mu.

The optical density of unirradiated crystals was studied in order to determine the change in optical density as the wavelength spectrum was scanned and also to see if any color centers or absorption peaks were present in unirradiated crystals. Irradiated crystals were studied to see what color centers are formed at room temperature exposure.

The first step revealed that the F-center is the most pronounced absorption peak present in the irradiated crystals. The difference or change in optical density between unirradiated and irradiated crystals at the wavelength of the F-center peak was found for various exposure doses. The relationship between radiation dose and change in optical density was determined in this manner.

The general annealing or recovery of irradiated crystals was also studied. Color centers are usually subject to optical and thermal bleaching at room temperature. The following method was adopted for the study of the process of annealing.

1) The optical density of the F-center peak was measured as a function of time, with the samples subjected to no illumination. In this case it is believed annealing of the color centers occurs by some thermal process.

2) The sample was illuminated with monochromatic light having the

wavelength of the F-center peak. The decrease in optical density as a function of time was measured. In this case, the F-center absorbs energy of a single frequency.

3) The sample was illuminated with white light. The color centers absorb light composed of photons of all wavelengths in the visible region.

A more detailed study of annealing in NaCl was also attempted. Identically irradiated crystals were illuminated with monochromatic light of different wavelengths. The decrease in the density of F-centers was studied as a function of the wavelength of the illuminating light. An illumination period of five hours was used for each trial.

Also, the change in the concentration of M-centers was studied. It is theorized that M-centers are a composite of an F-center and a positive-negative vacancy pair. It is thought that with a breakdown of F-centers there should then be an accompanying build up of M-centers.

Irradiated crystals were illuminated with a number of selected wave-lengths. The change in optical density of the F-center peak and the M-center peak was measured. This was done with a view to finding a correlation between the decay of F-centers and build up of M-centers.

RESULTS

The study of the optical density as a function of the wavelength is shown in Figures 4-6. It will be noted that for unirradiated samples the optical density is largest at the far edge of the ultra violet region, at 200 mu, and decreases smoothly as the spectrum shifts through the visible region. There are no absorption peaks present in the unirradiated crystals.

In each irradiated sample two absorption peaks appear. The most pronounced peak is identified as the F-center. The small peak towards the long wavelength side of the F-center is identified as the M-center. The wavelengths, at which the maximum of the absorption peaks occur, agree remarkably well with values listed by Klick (Schulman and Compton, 17, p. 29)(see Appendix). The values from this experiment are:

1) NaCl: F-center at 458 mu; M-center at 725 mu.

2) KCl : F-center at 558 mu; M-center at 825 mu.

3) LiF : F-center at 250 mu; M-center at 440 mu.

Figures 7-9 show the effect of the total radiation dose received by the crystals on the intensity of F-center formation. In Figure 7 the formation of F-centers, represented by the change in optical density, increases linearly with increasing radiation dose up to about 12,000 rads. At this dose (12,000 rads) there is a change in slope that continues to about 25,000 rads. Above 25,000 rads there is a second linear region. The slope of the first linear region is much steeper than in the second linear region which exists at the higher doses.

Figure 8 shows the change in optical density of KCl as a function of the total dose for two different dose rates. At the dose rate of
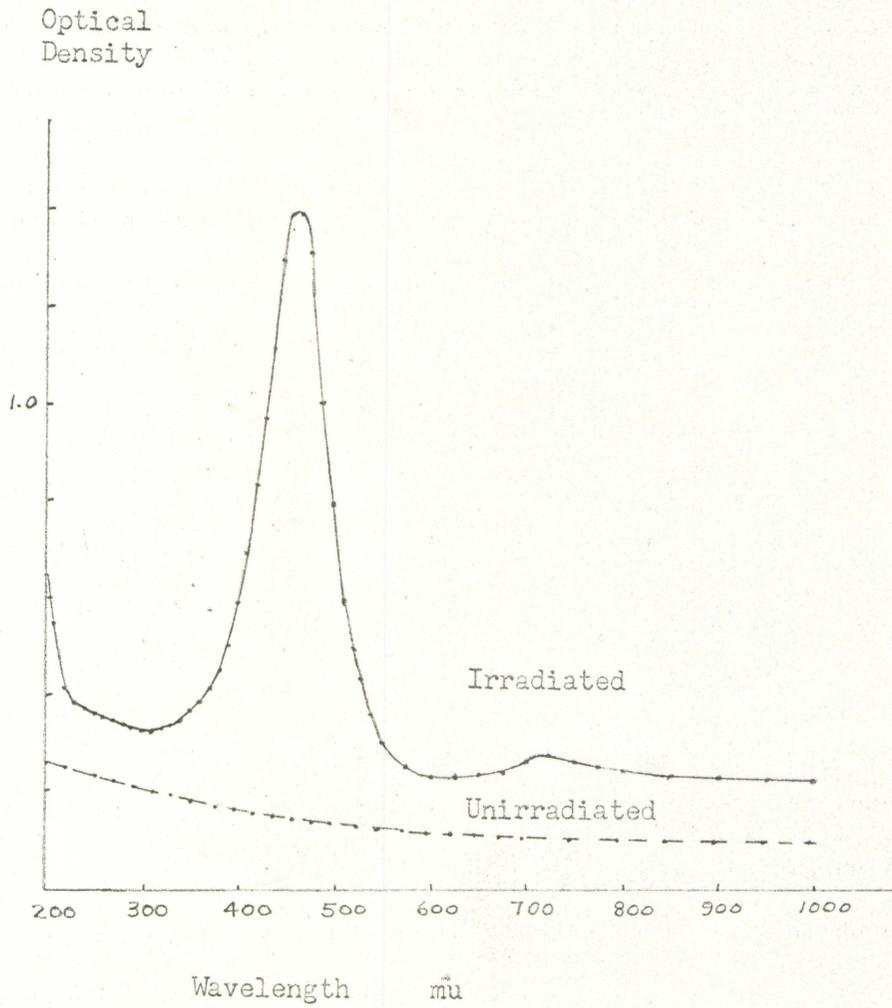
Figure 4. Optical density as a function of
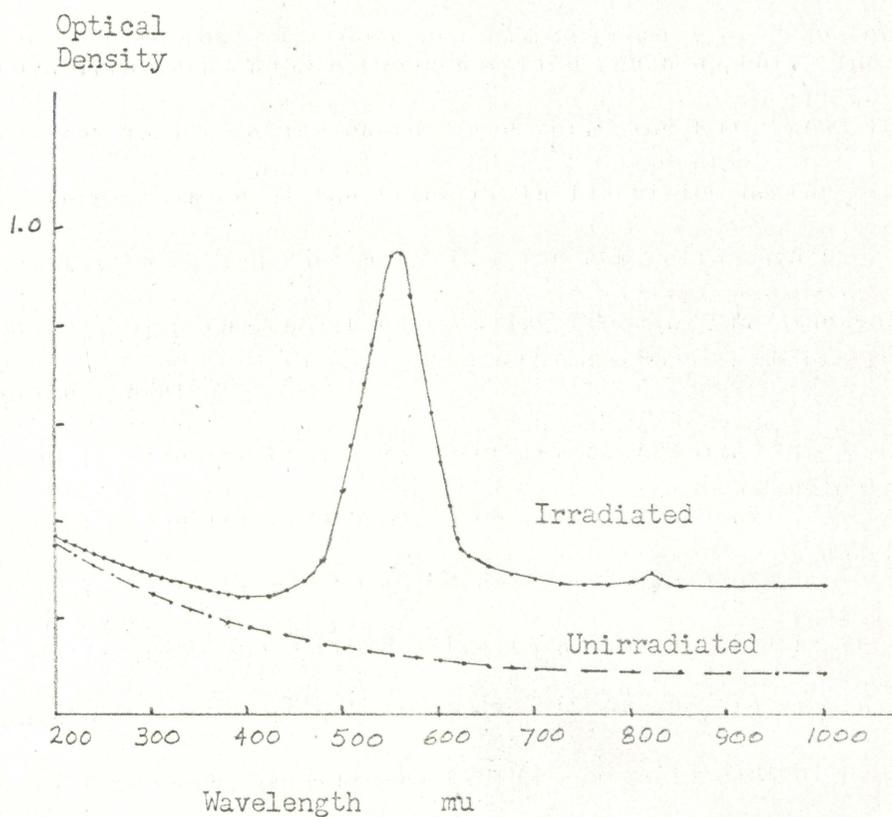wavelength in NaCl.

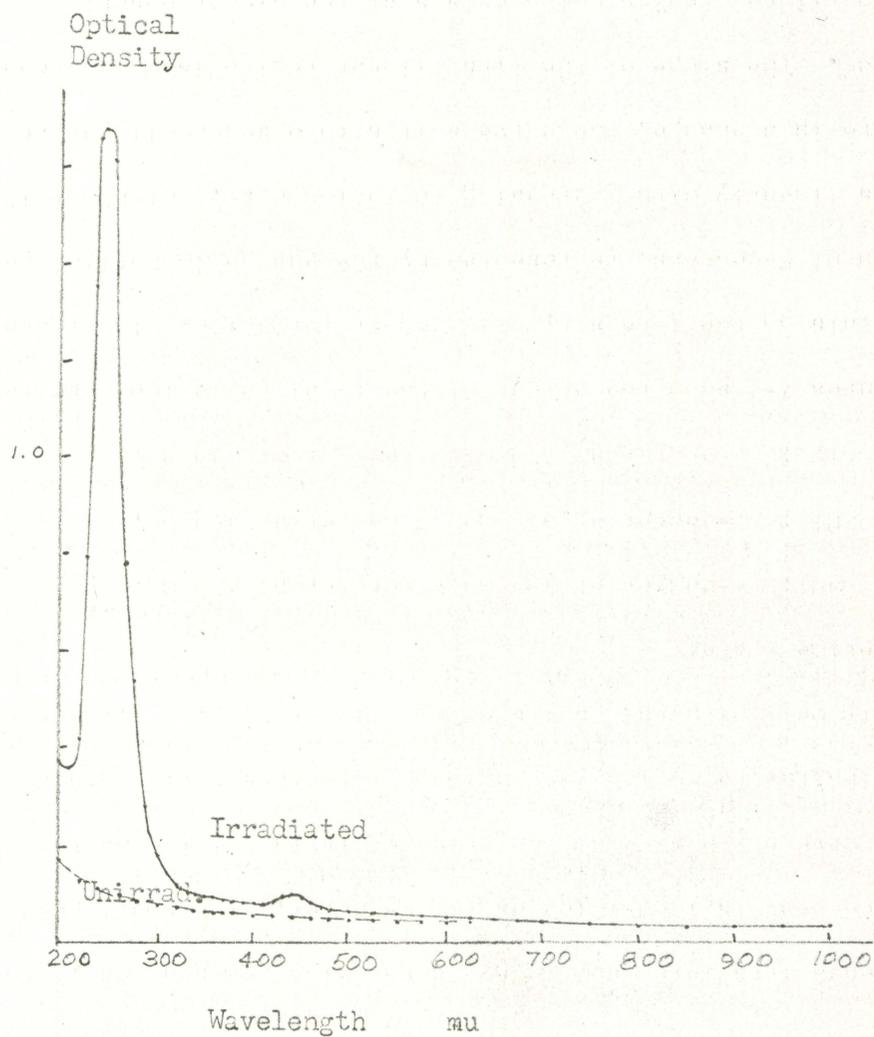Figure 5. Optical density as a function of
          wavelength in KCl.

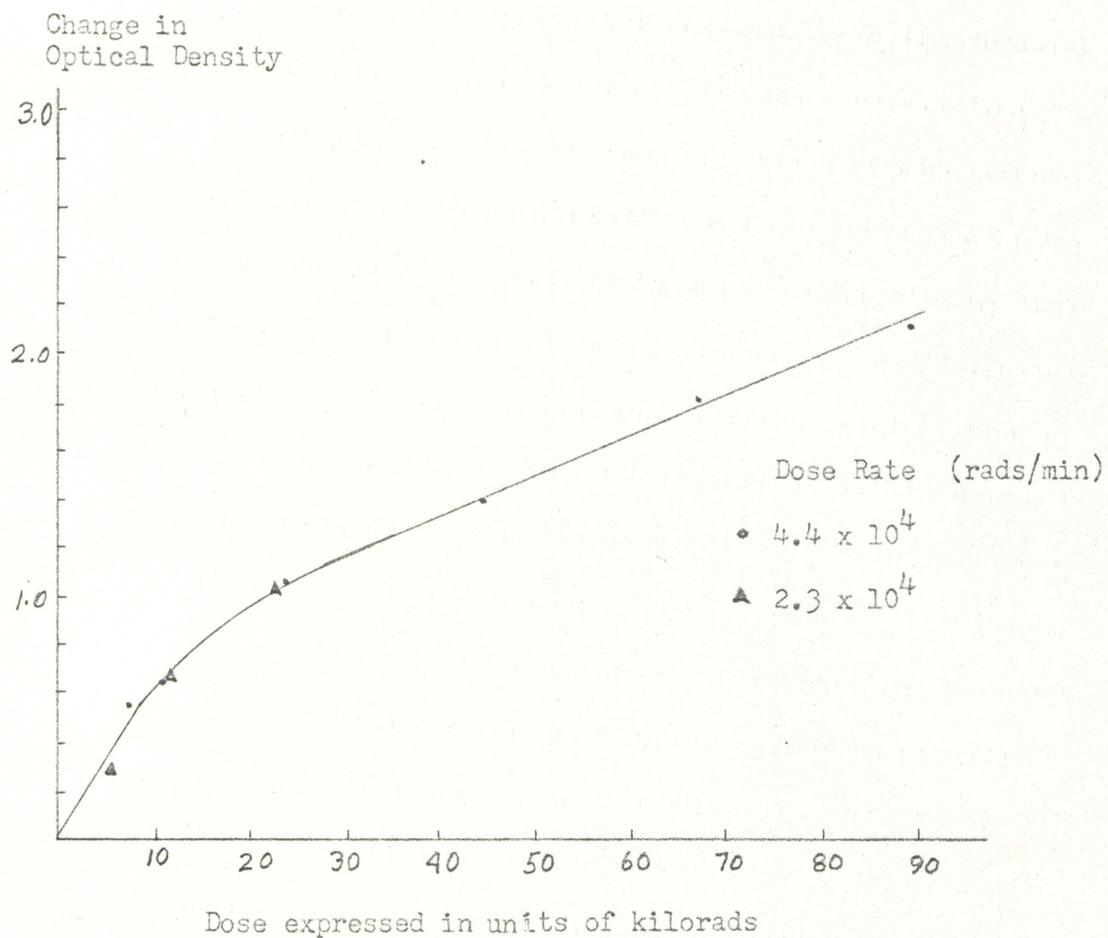Figure 6. Optical density as a function of
wavelength in LiF.

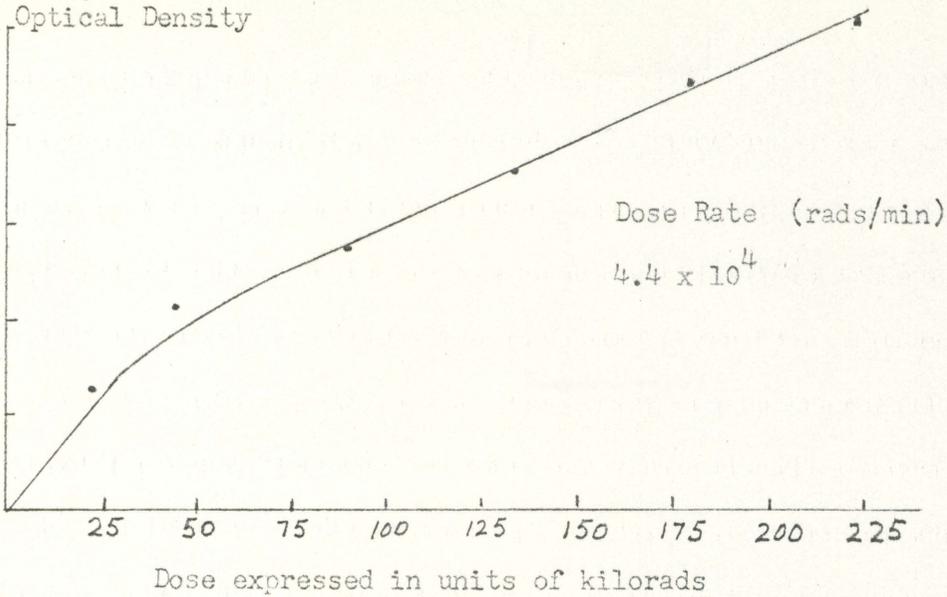Figure 7.   Change in optical density as a function of
irradiation dose in NaCl.

Change in
Optical Density

Dose Rate (rads/min)

4.4×10^{4}

Dose expressed in units of kilorads

Change in
Optical Density

2.0 —

Dose Rate (rads/min)

8.8×10^{4}

1.0 —

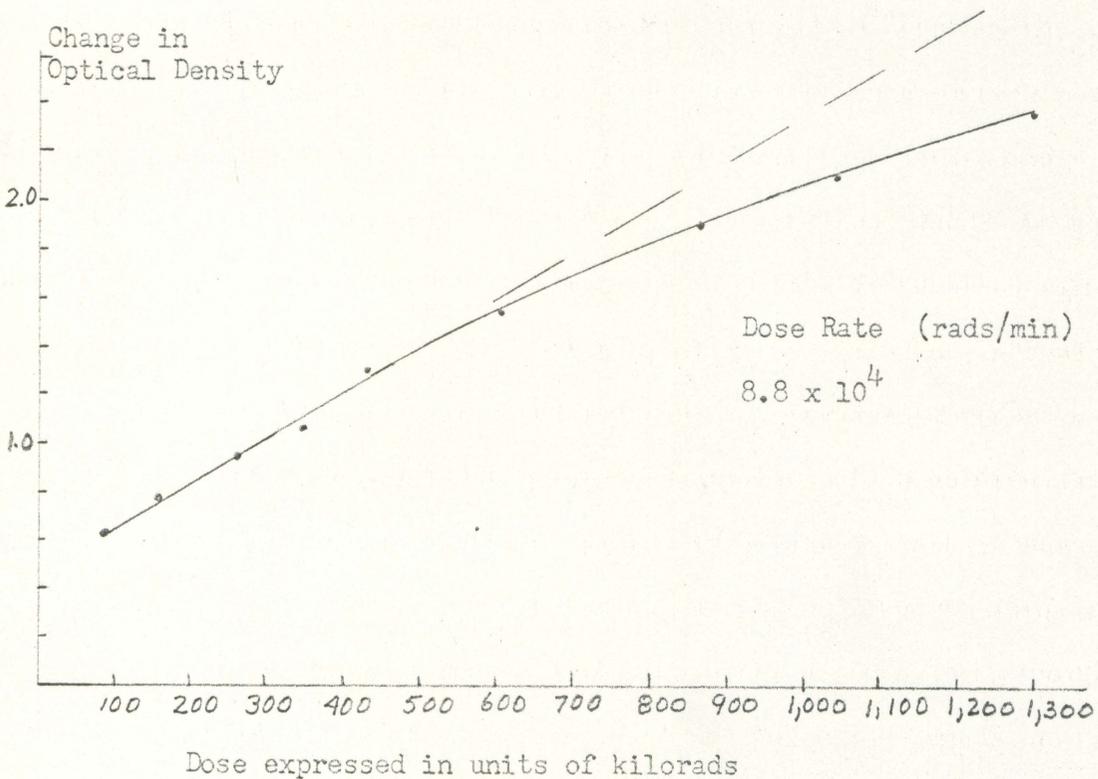Dose expressed in units of kilorads

Figure 8. Change in optical density as a function of
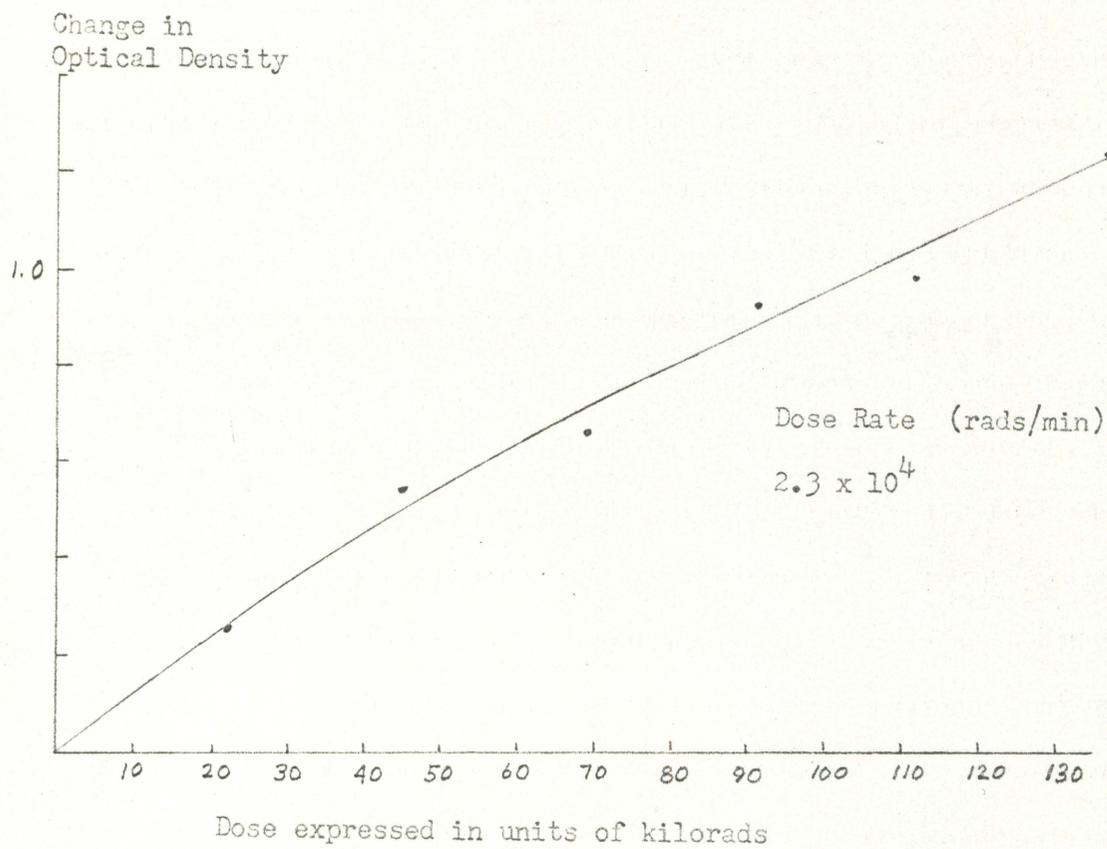irradiation dose in KCl.

Figure 9. Change in optical density as a function of
irradiation dose in LiF.

4.4 x 10^4 rad/min., there appears to be two linear regions with a change
in slope as found in NaCl. The exposure to a dose rate of 8.8 x
10^4 rad/min. shows that the relationship is initially linear but begins to
deviate at about a dose of 400,000 rads tending to approach some satura-
tion level. It is observed that in KCl the amount of coloration produced
is considerably greater when the crystal is exposed to a larger dose rate
than when exposed to the smaller dose rate even though the total dose
received by the crystals is the same. For example, at a total dose of
89,000 rads the change in optical density at the 4.4 x 10^4 rad/min. dose
rate is 0.275; while at the 8.8 x 10^4 rad/min. dose rate the change in
optical density is 0.617.

LiF shows the two linear regions of formation of F-centers although
the change in slope is very slight at the doses studied. This is seen in
Figure 9.

The results of the decay studies are shown in Figures 10-12. When
the crystals are exposed to no illumination it is assumed that the decreases
in F-centers occur by some thermal process. The decrease in optical
density over a 24 hour period is not very significant for thermal annealing
at room temperature, as Figure 10 shows. When the samples are illuminated
with monochromatic light of the same wavelength as the F-center absorption
peak (called F-light) the decay appears as shown in Figure 11. The effect
of F-light absorption is greater than for thermal annealing.

Figure 12 shows the decrease in optical density as a function of
exposure to white light. The crystals were removed from the spectropho-
tometer and exposed to room light for varying time periods. The entire
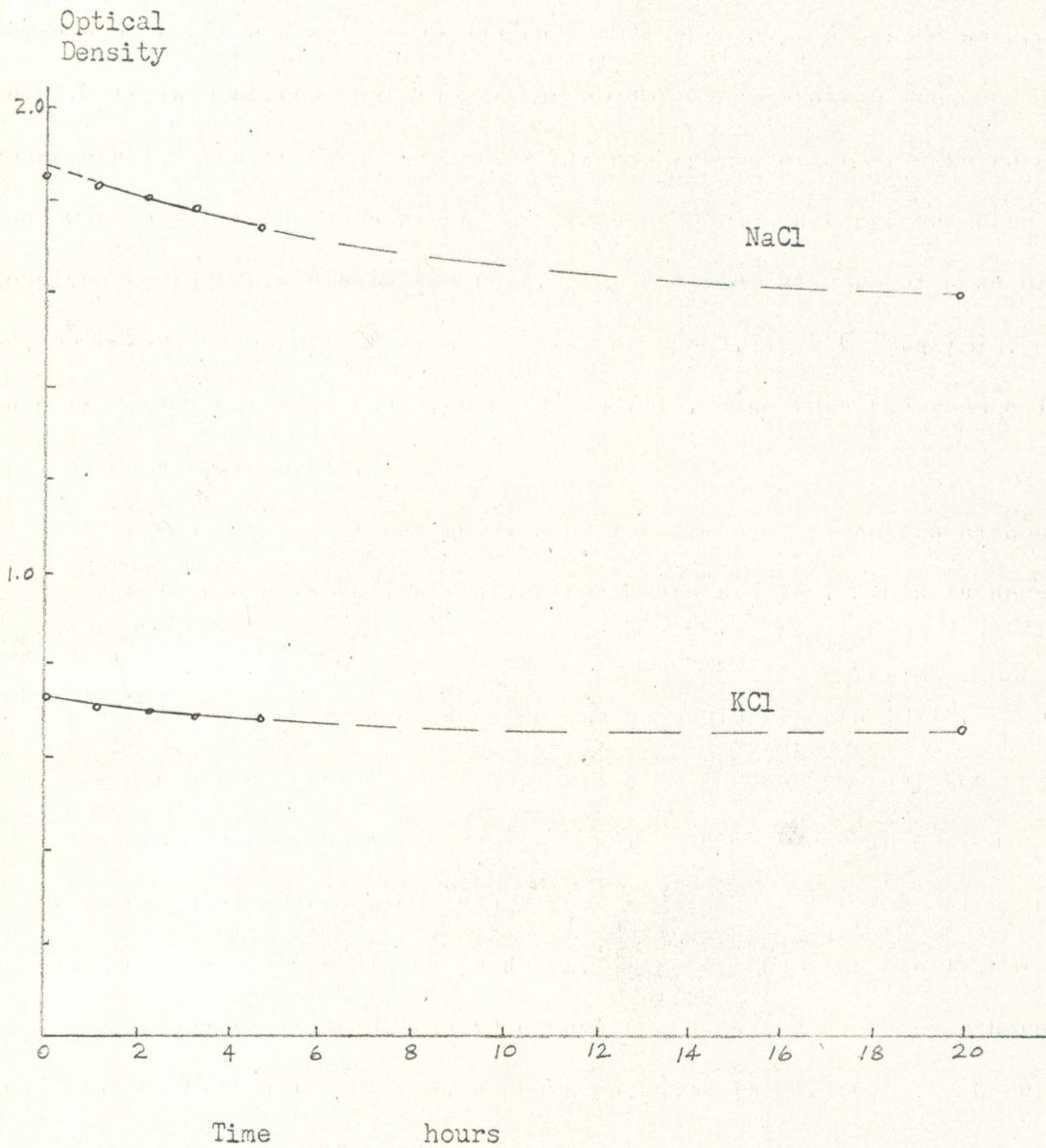
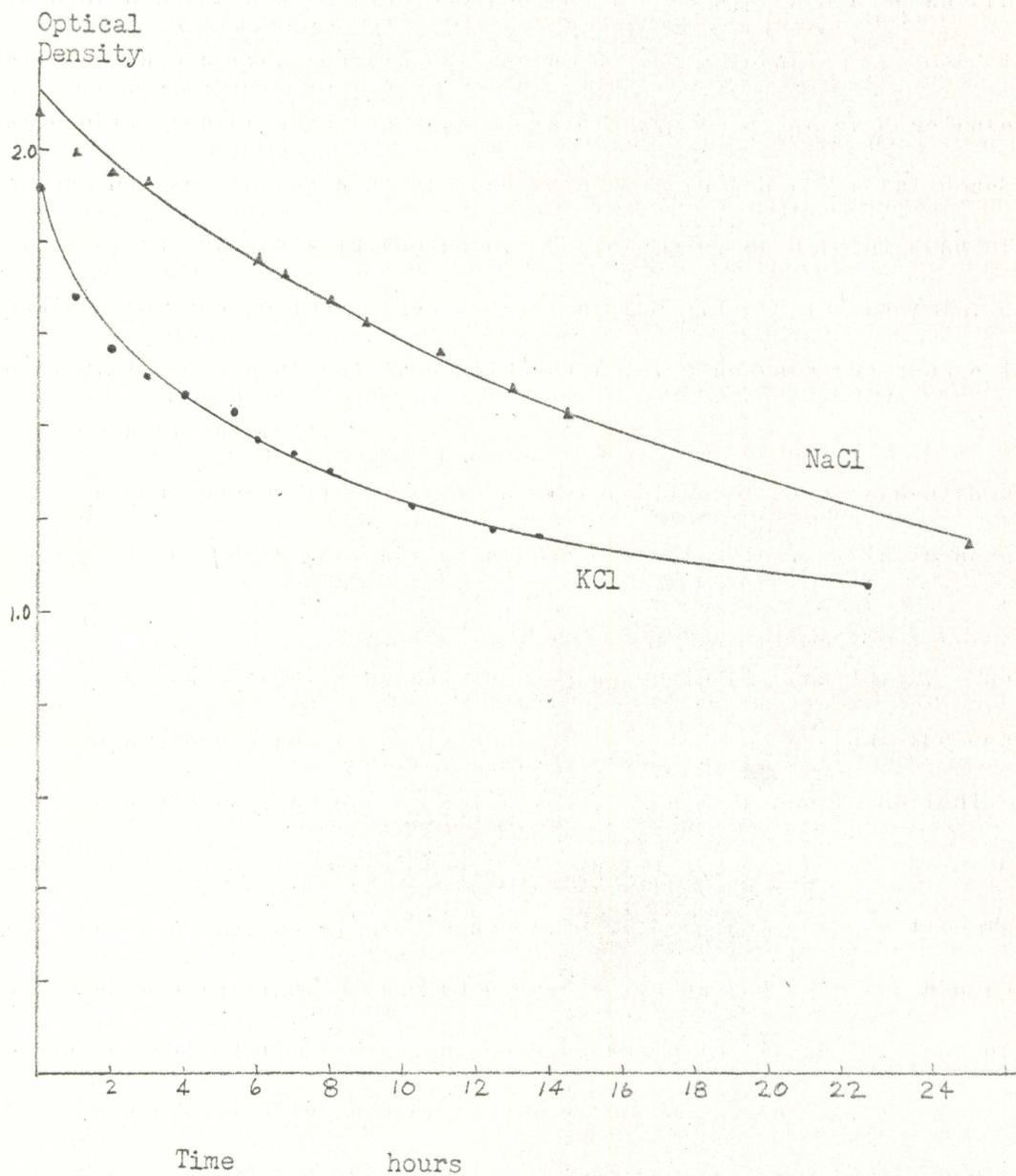Figure 10. Decay of F-center peak with no illumination.

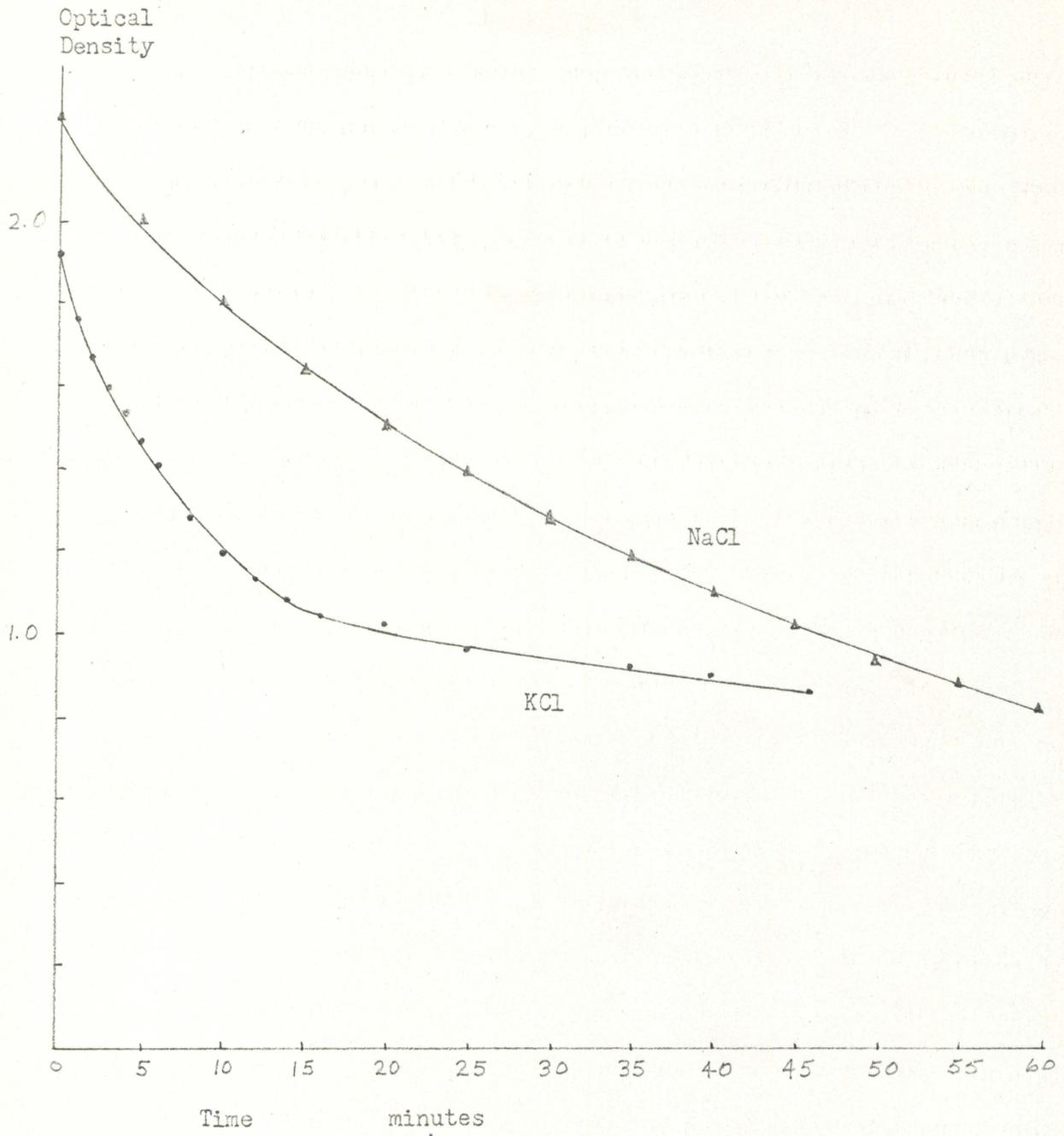Figure 11. Decay of F-center peak illuminated with F-light.

Figure 12. Decay of F-center peak illuminated with white light.

crystal is bleached in this case. For F-light bleaching, the small beam of light emerging from the monochromator illuminates the crystal so only a small part of the crystal's cross-sectional area is exposed. This accounts for the difference in the order of decay times. The optical studies show that annealing of color centers is a complex phenomena. Figure 13 shows that annealing in NaCl has an exponential component while in KCl there may be several exponential components present.

Color centers in LiF are exceptionally stable at room temperature. A period of days is required to notice a slight decrease in optical density of the F-center. LiF crystals were heated to 500° C. in order to bleach them.

The results of the study of the decay of F-centers and build up of M-centers in NaCl are shown in Figure 14. The change in optical density was determined. This is the change in optical density occurring during the illumination. The change in optical density of the F-center and M-center was measured for each wavelength used to illuminate the irradiated crystal.

As Figure 14 shows, the wavelength at which the greatest decrease in F-center concentration occurs correlates quite well with the positive change or increase in M-center concentration. The period of illumination probably is too short for the magnitudes of the fractional change to have much meaning.
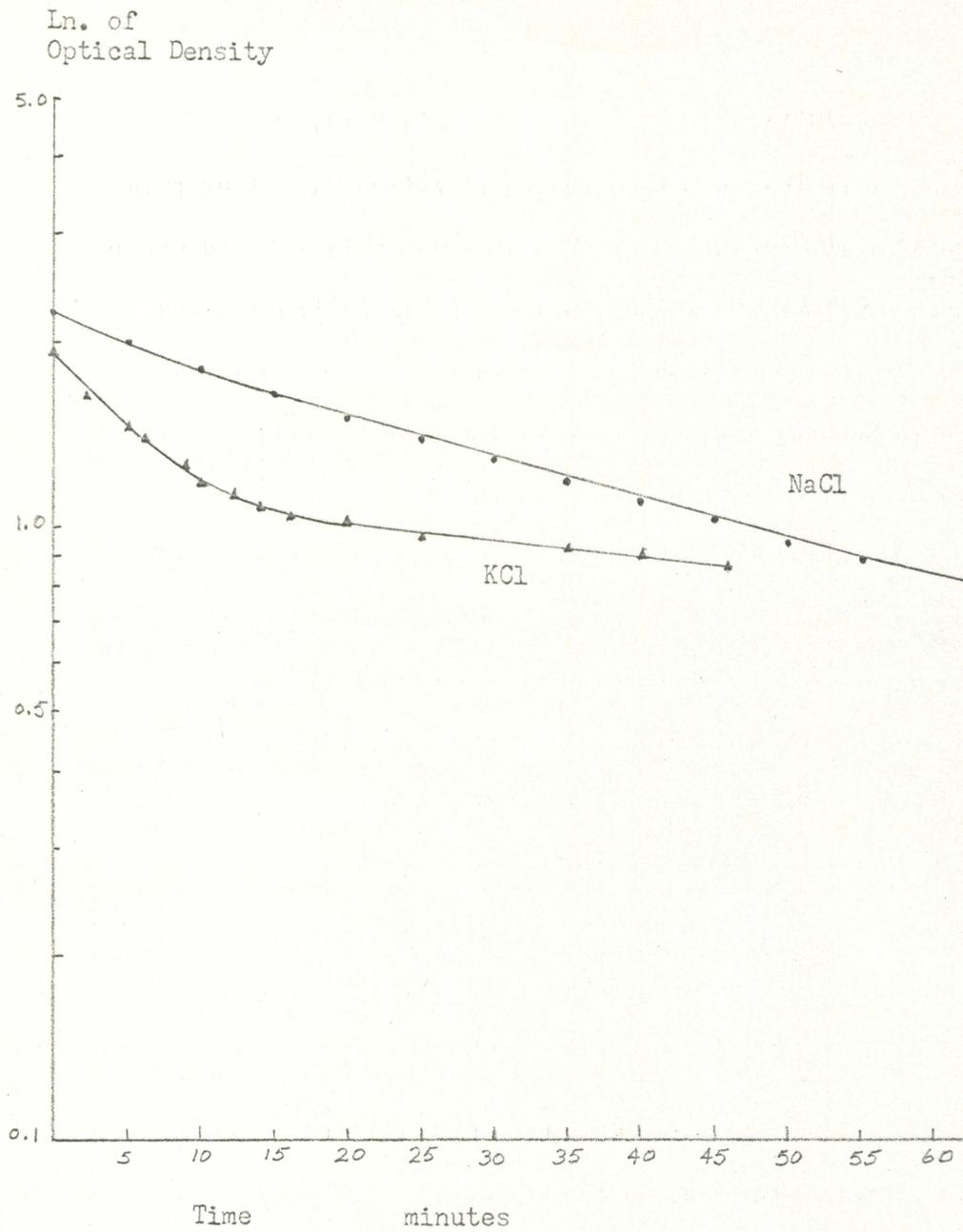
Figure 13. Plot of natural logarithm of optical density as
            a function of time. Illumination with white light.

Change in optical
density of M-center

Wavelength   mu

Decrease in optical
density of F-center

Wavelength   mu
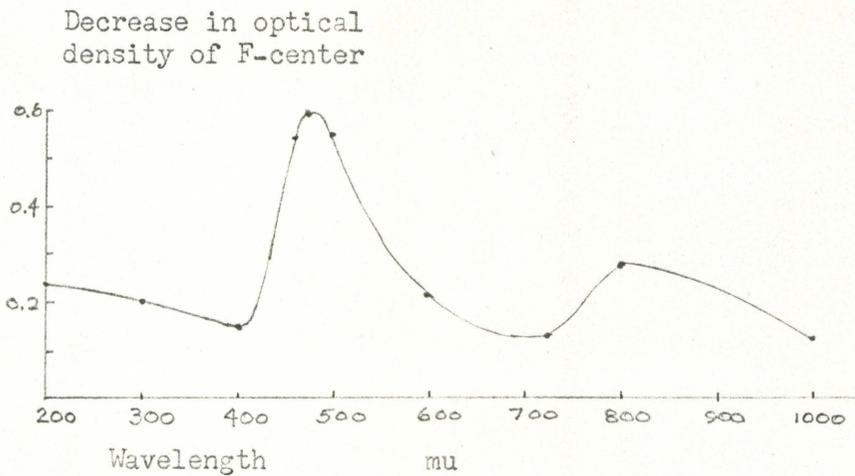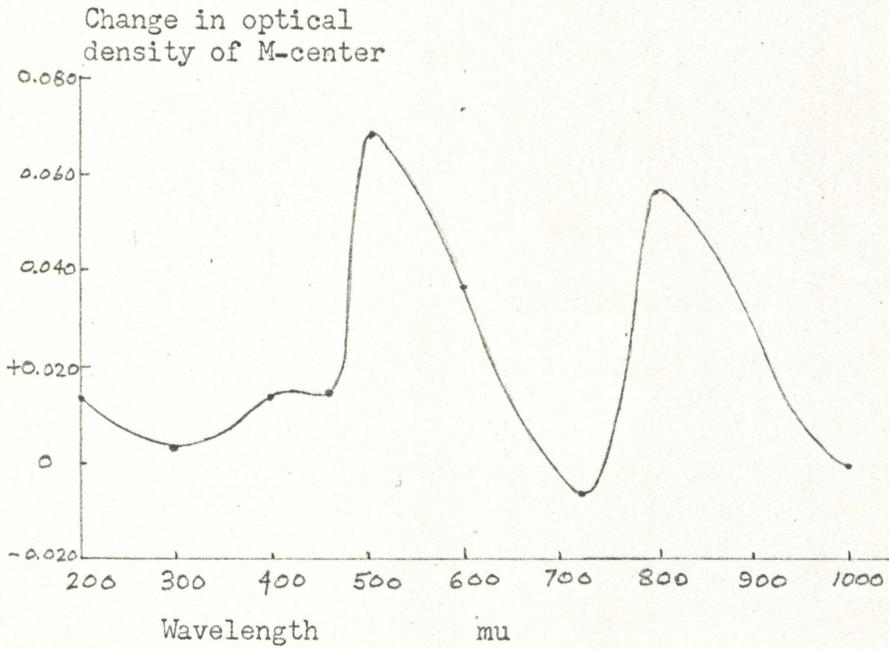
Figure 14.   Comparison of decrease in F-center peak and
             change in M-center peak as a function of the
             wavelength of illuminating or bleaching light.

CONCLUSIONS

The following conclusions may be drawn from this study.

1. The color centers observed with this experimental set up correspond very well with the work of others (see Appendix).

2. There appears to be sufficient mobility of defects that the more complex centers, such as the M-center, are formed in the irradiated crystals.

3. The rate of formation of color centers seems to follow the same pattern in each type of crystal. Initially there is a rapid linear formation of color centers. At larger irradiation doses the rate of formation decreases though it is still linear.

4. There is a difference in the ease of color formation. Color centers form much more readily in NaCl than they do in KCl and LiF. In KCl it is noticed that the change in optical density differs for different dose rates even though the total dose received is the same. It is probable that in the case of KCl the simultaneous formation and recovery occurring at the lower dose rate is more pronounced. This would account for the lower change in optical density at low dose rates.

5. The results in general indicate that the process of annealing in the materials and under the conditions used for bleaching is complex and needs a very systematic and thorough investigation. This comparative and qualitative study of the radiation effects in halides is exploratory in nature and is just a step in a more detailed systematic study of this phenomena.

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ACKNOWLEDGMENTS

APPENDIX

Dose Rate Calibration of Irradiation Positions

Run no.	Irrad. time	Dosimeter Optical Density Irrad.	Dosimeter Optical Density Unirrad.	Change in Optical Density	Dose rate 10^4 rad/min.

Source position setting of 40.20

Run no.	Irrad. time	Dosimeter Optical Density Irrad.	Dosimeter Optical Density Unirrad.	Change in Optical Density	Dose rate 10^4 rad/min.
1	10.30	0.558	0.019	0.539	8.6
2	10.35	0.587	0.019	0.568	9.0
3	10.25	0.568	0.020	0.548	8.8
4	10.25	0.562	0.020	0.542	8.7

Source position setting of 40.42

Run no.	Irrad. time	Dosimeter Optical Density Irrad.	Dosimeter Optical Density Unirrad.	Change in Optical Density	Dose rate 10^4 rad/min.
1	20.15	0.557	0.020	0.537	4.4
2	20.20	0.576	0.020	0.556	4.5
3	20.20	0.551	0.021	0.530	4.3
4	20.20	0.572	0.021	0.551	4.5

Source position setting of 40.72

Run no.	Irrad. time	Dosimeter Optical Density Irrad.	Dosimeter Optical Density Unirrad.	Change in Optical Density	Dose rate 10^4 rad/min.
1	40.25	0.571	0.022	0.549	2.2
2	40.25	0.588	0.022	0.566	2.3
3	40.15	0.586	0.021	0.565	2.3
4	40.20	0.576	0.021	0.555	2.3

Averaged values

Position	Dose rate (rad/min.)
40.20	8.8×10^4
40.42	4.4×10^4
40.72	2.3×10^4

Absorption Peaks in Irradiated Crystals

Crystal	Center	Experimental value (mu)	Klick's value (mu)	Mador et al. value (mu)
NaCl	F	458	458	464
	M	725	725	725
KCl	F	558	556	
	M	825	825	
LiF	F	250	250	248
	M	440	444	450