

**RADIATION EFFECTS ON NATURAL ROCK SALT FROM  
"PROJECT SALT VAULT," LYONS, KANSAS**

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by

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**B.S., Kansas State University, 1971**

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**A MASTER'S THESIS**

**submitted in partial fulfillment of the  
requirements for the degree**

**MASTER OF SCIENCE**

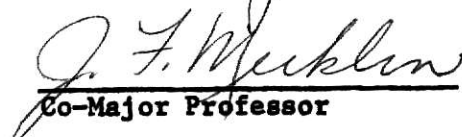
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**1973**

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## I. INTRODUCTION

The search for a place to store radioactive wastes, such as in NaCl (rock salt), has initiated this research on some aspects of the radiation effects on natural rock salt.

An important factor to be examined before storage of radioactive wastes in salt can be initiated is the degree to which heating and irradiation cause major changes (damage) in the rock salt.

Irradiation of solids, such as rock salt, results in the introduction of defects and other disorder to the crystal structure and, subsequently, stored energy. Stored energy refers to energy which will give a negative contribution to the specific heat of the solid when the latter is warmed subsequent to the irradiation.

With the exception of Cu and graphite, very few measurements have been made of stored energy in solids (1). Kobayashi reports an energy release of 2 to 2-1/2 cal/g between room temperature and 400°C in NaCl that had been heavily irradiated with protons at room temperature (1). Bunch & Pearlstein (2) have compared the F-center concentration in x-ray irradiated NaCl with the stored energy. For a saturation concentration of  $2 \times 10^{19}$  F centers/cm<sup>3</sup>, this would yield a saturation stored energy of 4 cal/g. At doses up to  $10^{11}$  rad, no more than 2 to 3 cal/g can be stored in rock salt (1). "It is clear that the stored energy saturates with dose and preliminary data suggest that stored energy behaves with respect to irradiation conditions in a fashion similar to that of F-center production. That is, the energy storage becomes greater as dose rate is increased or the sample temperature during irradiation is lowered" (1).

Stored energy release to some extent might be correlated with measured changes in optical absorption (1) of the crystal (rock salt plates). Defect centers, which give rise to optical absorption in a normally transparent spectral region, are called color centers (3,4). Most defects in pure alkali halides consist of alkali and halide ion vacancies. Passage of ionizing radiation through the crystal (rock salt) releases electron-hole pairs. Color centers are formed by the trapping of these charges at the defect or impurity sites. A schematic representation of the important color centers formed in alkali halides is shown in Fig. 1. A brief discussion of these centers, optical absorption, thermoluminescence and some closely related terms are given below.

#### Traps:

An ideal crystal is one which has no imperfections. Studies have shown that most real crystals do have imperfections and therefore do not have an ideal structural form. Natural rock salt crystals have a large number of imperfections and defects. These imperfections cause localized centers of positive or negative charge which are capable of trapping electrons or holes. These centers are called traps.

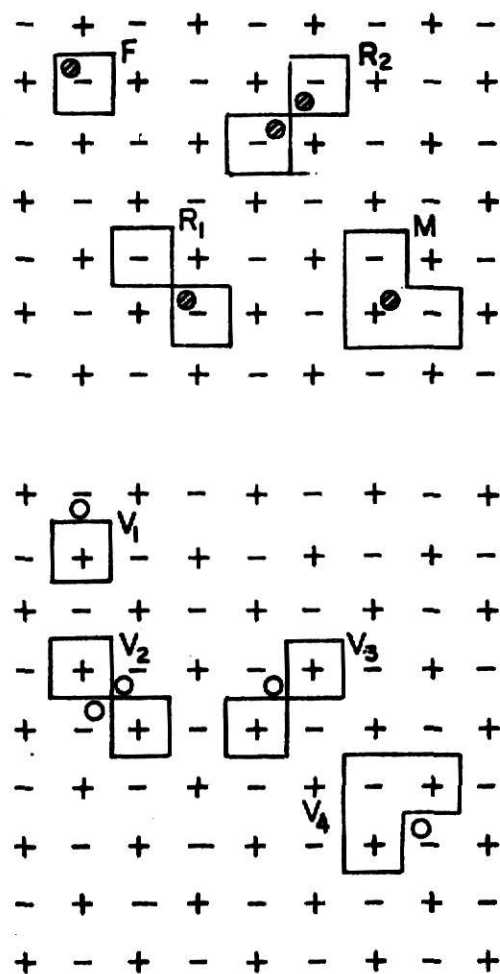
#### Trap Depth:

An ideal crystal does not have electrons whose energy states lie in the gap between the valence band and the conduction band (forbidden energy gap). Imperfect crystals (like rock salt), however, have traps whose energy states lie in the forbidden energy gap. An electron can be removed from the trap by exciting the electron to the conduction band and the

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+ = Alkali ion  
 - = Halogen ion  
 ● = Electron  
 ○ = Hole

Fig. 1. A schematic representation of the important color centers in alkali halides. (After reference 6.)

electron can recombine with a hole. The energy required to release the electron or hole from a trap, corresponds to the trap depth. The difference in the energy states of the conduction band and the trapped energy state is the energy needed to free the trap,  $E_t$ .

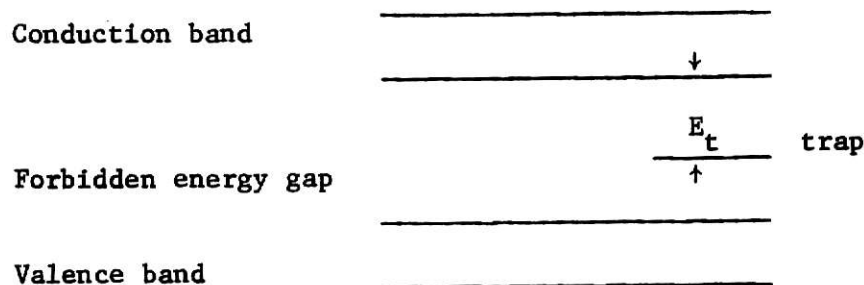


Fig. 2. Energy band model of a crystal

#### Thermoluminescence:

The bleaching of color on heating the irradiated crystal (plates) is due to the recombination of the thermally released charges from their traps. The recombination, and/or release of stored energy, is in some cases accompanied by the emission of visible light. This emission of light on heating the irradiated crystal (salt plate) is termed thermoluminescence, TL. A plot of thermoluminescent intensity versus temperature taken at a constant heating rate is called a glow curve.

#### Absorption:

The passage of ionizing radiation through sodium chloride and other minerals may cause color centers (3). This production of color has been known to result from the trapping of holes and electrons, released by ionizing radiation, at crystal imperfections and impurity sites which are called traps. The defect centers, formed by the trapped electron or hole, have excited states. Such defect centers, which give rise to optical

absorption in a normally transparent spectral region, are called color centers. The study of optical absorption spectra of crystals after irradiation provides an important tool in the identification of the defect centers giving rise to color in the crystals. The quantity to be measured is the optical density or the absorbance  $A$  (5).

$$A = \log_{10}(I_0/I)$$

where

$I_0$  = intensity of the light incident on the crystal,

$I$  = intensity of light transmitted by the crystal.

The absorption constant  $\alpha$  is given by:

$$\alpha = [\log_e(I_0/I)]/X$$

where

$X$  = optical path length.

#### The F Center:

Absorption of ultraviolet radiation or gamma rays leads to the excitation of electrons from the valence band to the conduction band. An electron thus set free, wanders in the crystal and can be trapped at a halogen ion vacancy. Such a center resembles a hydrogen atom and is called an F center (3,4). The ground and excited states of this center are localized energy levels in the forbidden energy gap of the crystal. The transition from the ground state to the first excited state on absorption of light gives rise to the F-center absorption band. In NaCl (rock salt), the F-center absorption band at 465 nm (2.67 eV) is the most prominent band to be observed on room temperature irradiation with gamma rays (2,3,4,6,7).

### M and R Centers:

On prolonged gamma irradiation, absorption bands on the low energy side of the F-center absorption band are observed. In NaCl (rock salt) an absorption band at 720 nm (1.722 eV) labeled as the M-center absorption band and absorption bands at 550 nm (2.25 eV) and 600 nm (1.97 eV) labeled as the  $R_1$ -center and the  $R_2$ -center absorption bands have been observed (3,4,6,7). The M and R centers have been interpreted as coagulation products of the F center due to migration of lattice defects (3,4). The  $R_1$  and  $R_2$  band arise due to transitions of the R center.

### $C_1$ - Colloid Center:

NaCl (rock salt), which has been "heavily irradiated" with gamma irradiation and then heated in the temperature range 160-200°C, turns blue. The absorbance of such a crystal shows a single band with its peak located about 560 nm (2.214 eV). This peak has been identified as the  $C_1$  peak (4,6,7). Pappu & McCarthy (7) have proposed a mechanism for colloid evolution in additively colored crystals, namely, that neutral F centers agglomerate via a vacancy diffusion mechanism and when the agglomerate of F centers attains a critical size the F-center electrons enter the valence levels of the alkali ion to form alkali metal atoms. This mechanism might be also valid in the case of irradiated crystals. The F-center concentration per se does not seem to be a significantly important factor in the evolution of  $C_1$  centers (7). It appears that the presence of second (or slow) stage F centers (implying therefore the presence of lattice damage done by irradiation) and the electron-hole recombination process have significant influence on the  $C_1$  center formation in irradiated crystals (7).

### V Centers:

Trapping of holes formed by the passage of radiation through the crystal gives rise to the trapped hole centers. Trapped hole centers are generally denoted as V centers. The V centers generally result (3) from the incorporation of halogen molecules or molecular ions in the lattice. Seitz (6) suggests that the  $V_3$  center is the inverse of the  $R_1$  center, the  $V_2$  the inverse of the  $R_2$  center, and the  $V_4$  center the inverse of the M center.

### Statement of the Problem

J. Bunch and E. Pearlstein (2) have related to some extent the stored energy in NaCl with the F-center production. By measuring the change in the peak-height of the F-center absorption band, and measuring the stored energy by solution calorimetry a similar correlation between F-center concentration ( $\propto$  peak height) and stored energy might be made for natural rock salt. The growth of the F-center absorption band as a function of irradiation temperature will also be examined. The behavior of natural rock salt thermoluminescence will also be studied as a function of dose.

All irradiations were done with a  $^{60}\text{Co}$  gamma source, with a dose rate of approximately 33.1 rads per second.

## II. EXPERIMENTAL PROCEDURE

The preparation and irradiation of the natural rock salt from the A.E.C. "Project Salt Vault" at Lyons, Kansas, are outlined in this chapter. The procedures are so chosen to allow for both thermoluminescent and optical absorption measurements to be made on the same sample.

### Cleaving of Rock Salt Plates

Two cylinders, (1-foot in diameter and approximately 8 inches high) of natural rock salt have been obtained from "Project Salt Vault." These cylinders are representative of the rock salt in the Lyons, Kansas mine.

In order to assure that all samples have similar composition, all plates were cleaved from adjacent areas on one of the cylinders. The important criteria was that the plates be at least 3 mm in width and 11 mm in height, which was the maximum dimensions of the light beam used in the optical absorption measurements. The thickness of the plates varied from 1 mm to 3.5 mm. The thickness of the plate was found by averaging the thickness at each end of the plate.

### Irradiation of Samples

Gammacell-220 of the Atomic Energy of Canada was used to irradiate the samples. The Gammacell was loaded with a 3,963 curie  $^{60}\text{Co}$  source on March 15, 1965. The source was in the form of a hollow circular cylinder located inside a thick water shield. A 6 inch diameter by 8 inch high irradiation chamber was located in a plunger. The plunger was lowered mechanically into the middle of the radiation source. The plunger was operated by an electric timer. The desired time of irradiation may be preset on the timer in seconds, minutes, or hours.

A 1/2-inch polyethylene disc was made to fit in the irradiation chamber of the Gammacell by Kaiseruddin (8). Kaiseruddin determined from the iso-dose curves for the chamber, supplied by Atomic Energy of Canada, the positioning of samples, in the chamber, such that they receive the same dose as if they had been placed at the center of the chamber. This position was 2-3/4 inches above the base of the chamber and was 2 inches away from the central axis of the chamber. The dose rate at this position was 33.1 rad/sec.

The natural rock salt plates were weighed on an analytical balance, for identification purposes, before placing them in 30 ml glass vials. The glass vials were then placed on the polyethylene platform and centered so that the center of the vial was located 2 inches away from the central axis of the irradiation chamber. The chamber was then lowered and irradiation of the rock salt was carried out for the preset time at 23°C. Since other projects required the use of the Gammacell, the highly irradiated samples (time of irradiation greater than 20 hours) were not irradiated continuously.

#### Absorption Measurements

Optical absorption measurements on the natural rock salt plates were made using a Model 14 Cary Recording Spectrophotometer (see Fig. 3 for schematic of the optics). The Model 14 spectrophotometer automatically records the absorption spectrum in the wavelength region of 185 nm to 2600 nm with good resolving power and high photometric accuracy.

To be certain that the crystals were in the light beam of the Cary 14 spectrophotometer the wavelength was set at 520 nm (green) and the slit completely open (3 mm). In this position, the light beam can be seen and the

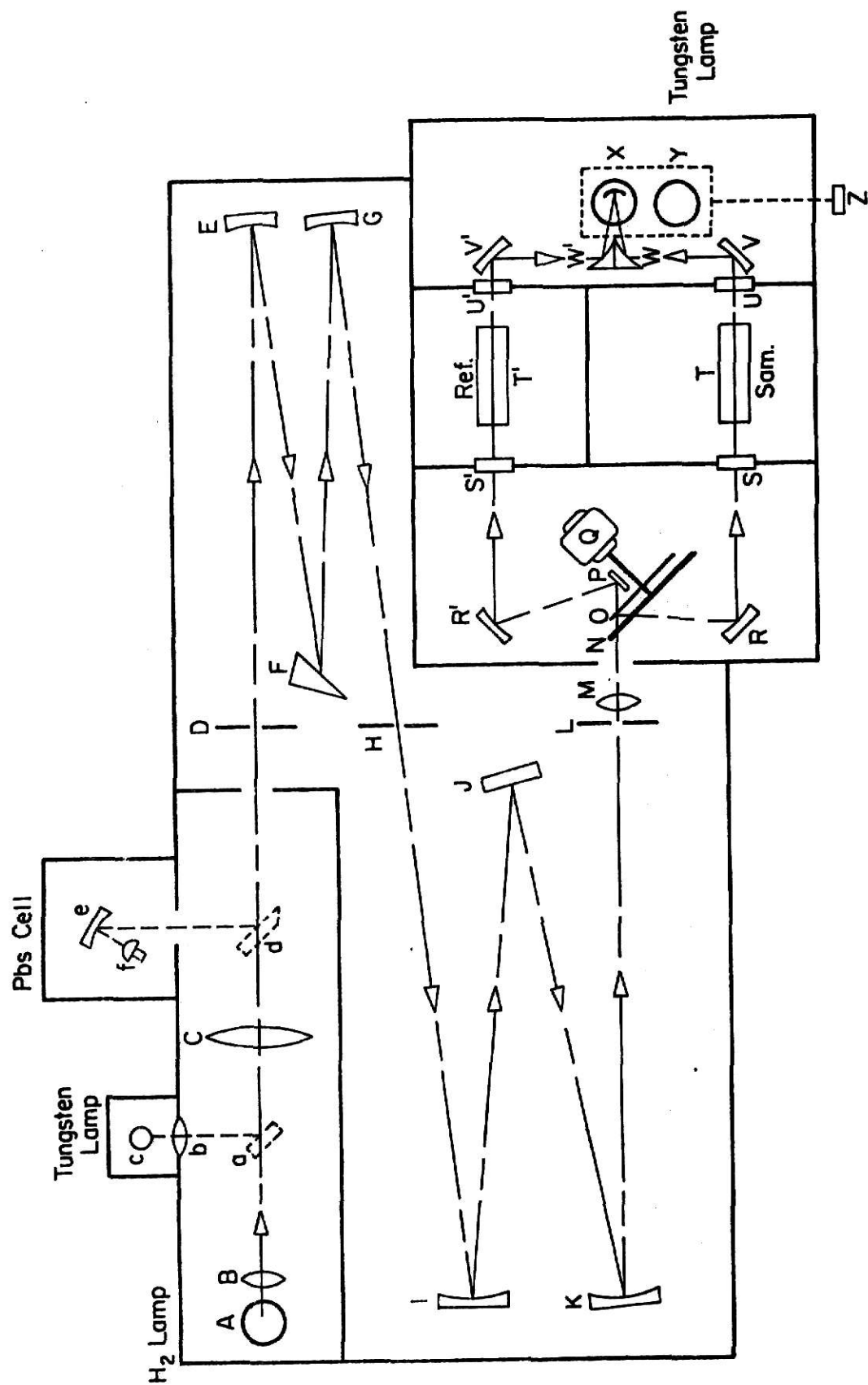


Fig. 3. Schematic of the optics for the Model 14 Cary Recording Spectrophotometer. (After reference 9.)



extreme left edge of the light beam was marked on the sample holder. The left side of all samples were then placed at this mark when absorbance measurements were to be made.

An absorption spectrum was taken of each plate before and after irradiation. Each absorbance measurement of the plate was made with air in the reference compartment of the spectrophotometer. None of the plates, irradiated or unirradiated, had any observable absorption peaks in the near infrared. Therefore, all absorption spectra on the plates were from 185 nm to 800 nm.

#### Powdering the Irradiated Crystals for Thermoluminescent Measurements

After the final absorption spectra were taken on the irradiated rock salt plates, each plate was powdered. The powder was then sieved through a #50 and #60 U.S. Standard sieve with openings of .0117 inches and .0098 inches or 297 microns and 250 microns, respectively. The particle size of the powdered salt used in thermoluminescent measurements was less than 250 microns. After each plate was powdered and sieved, the mortar and pedestal were wiped with a clean Kaydry towel and the sieves and funnel were flushed with compressed air to remove any salt before proceeding to the next sample.

#### Thermoluminescent Measurements on the Powdered Rock Salt

The reader unit to be used to measure the thermoluminescent output was a TLD system set up for spectrum measurements using an EG and G Model 2010 A programmer, an EG and G Model 2020 A Read Head, an EMI 9734 B-5465 photo tube, a Varian Series G-1000 Strip chart recorder and a Keithley 410 micro-microammeter. A block diagram of the readout system for thermoluminescent samples is shown in Fig. 4.

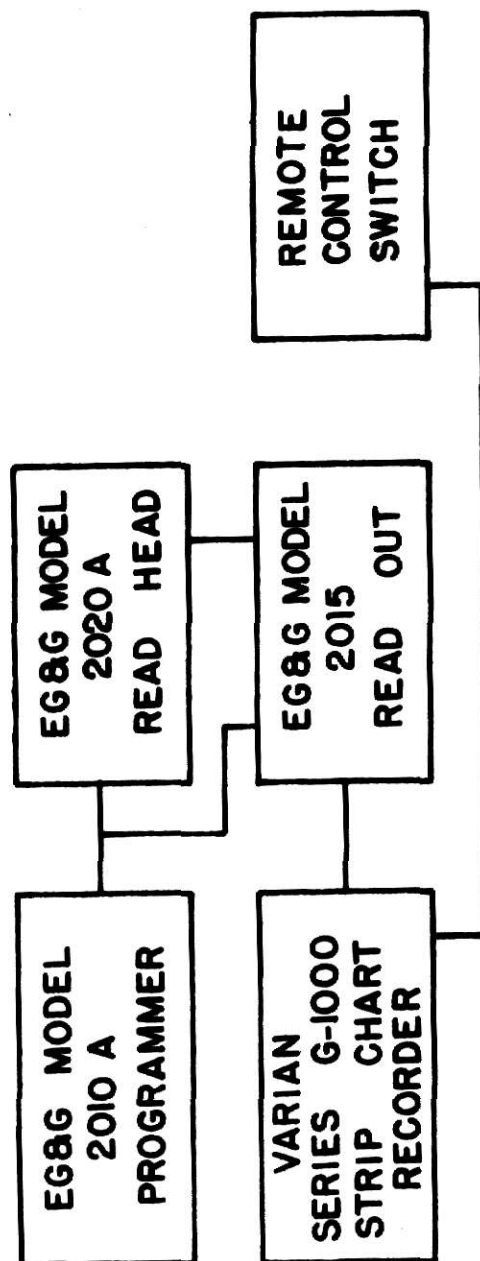


Fig. 4. Block diagram of the readout system for TL samples.

A small quantity of the powdered irradiated rock salt was placed in an aluminum holder. The holder is approximately 11 mm in length and 10 mm in width. It has a 3/8 inch wide circular depression for the powdered samples to be placed in. The aluminum holder fits on top and against the heating planchet of the 2020 A Read Head.

The thermoluminescent responses were measured and the aluminum holder and powder were weighed on an analytical balance from which the amount of powdered rock salt was obtained. Once the weight of the powdered salt was obtained, it was discarded. The thermoluminescent response was then found per gram of powdered rock salt read.

#### Effect of Temperature

The rock salt plates used in this irradiation temperature study were obtained in a manner described in Cleaving of Rock Salt Plates. A number of unirradiated rock salt plates were heated at 400°C for 1 hour and allowed to cool in the open air. As a result of heating, many of the crystals either shattered due to escaping water vapor or have raised protrusions. Five of the best rock salt plates, as far as optical absorption properties and uniform thickness were concerned, were chosen for use in the irradiation temperature study. These same five plates were used over again for the next irradiation after 1 hour annealing at 400°C.

An oven was made by wrapping asbestos around a 10 cm glass tube, then wrapping with nichrome wire and finally another layer of asbestos. A variable power supply was used to obtain the desired temperature. The temperature was measured by means of a copper constantan thermocouple cemented to the bottom of the glass tube. To prevent the heating of the gammacell chamber, the chamber was lined with a 3/4 inch piece of insulation backed with a heat shield. The rock salt plates were placed, on the

bottom of the oven, so that the crystals were 2-3/4 inches above the bottom of the irradiation chamber and centered radially.

The crystals were allowed to reach equilibrium in the oven before they were lowered into the irradiation source as previously described in Irradiation of Samples.

The samples were irradiated for 64 minutes at the appropriate temperature. At the end of the irradiation, the rock salt sample-plates were immediately removed and placed on a piece of metal at room temperature.

Crystals were annealed for 1 hour at 400°C in a Dubuque IV type 10500 furnace and allowed to cool in air to room temperature, before being re-irradiated. Bunch and Pearlstein (2) report that annealing restores a NaCl sample to its preirradiated condition. An absorption spectrum after annealing has confirmed this to be true for natural rock salt plates.

#### Heating 500 Hour Irradiated Rock Salt

A 30 ml glass vial was filled with chunks of unirradiated natural rock salt from the Lyon's mine and irradiated for 500 hours ( $59.5 \times 10^6$  rad) in the Gammacell. Small pieces of the rock salt were placed in a beaker and heated in a Dubuque IV type 10500 furnace at the following temperatures for 5 minutes: 96°C, 146°C, 171°C, 186°C, 196°C, and 221°C. One piece of salt was removed after each successive heating.

#### Heating Royal Blue Salt from Project Salt Vault

A piece of irradiated violet blue rock salt obtained from the "Project Salt Vault" had a copper-constantan thermocouple cemented in the middle of the sample. This sample was placed in a Dubuque IV type 10500 heating furnace and the temperature recorded when the violet blue color began to disappear.

### III. RESULTS AND DISCUSSION

#### F-Center Absorbance

Five natural rock salt plates were irradiated at a dose rate of  $1.2 \times 10^5$  rad/hr to doses ranging from  $.06 \times 10^6$  to  $67.37 \times 10^6$  rad. Rock salt plates irradiated in this range were light yellow to a dark orange brown in color.

There are two peaks in the absorption spectrum at low doses. One peak, the F-center absorption band, is at 465 nm (2.67 eV) and the other peak, the M-center absorption band, is at 720 nm (1.71 eV) (2,3,4,6). At high doses ( $> 1.19 \times 10^6$  rad), an absorption band at 600 nm (2.0 eV) is observed. This band is ascribed to an  $R_2$  center (3,4,6). A typical absorption spectrum of a rock salt plate that has been irradiated to a dose of  $.595 \times 10^6$  rad and  $67.37 \times 10^6$  rad is shown in Fig. 5. The peak heights at 465 nm (2.67 eV) and at 720 nm (1.71 eV) are listed in Table I as a function of the dose and shown in Fig. 6. This spectrum agrees with absorption spectrum of pure NaCl (Harshaw) samples, irradiated with  $^{60}\text{Co}$   $\gamma$  rays for 200 hours at  $10^6$  rad/hr (2).

The concentration of F centers is beginning to saturate at about  $6 \times 10^5$  rad while the concentration of M centers is still growing at  $67.37 \times 10^6$  rad. This growth and saturation of the F-center concentration is similar to what P. L. Mattern, K. Lengweiler, and P. W. Levy (10) have observed. They obtained their curve by irradiating Harshaw NaCl at room temperature with a  $^{60}\text{Co}$   $\gamma$  source at a dose rate of  $10^5$  rad per hour. For their Harshaw NaCl, they found that the F-center production starts saturating at  $2 \times 10^5$  rad. No information was given regarding the M center.

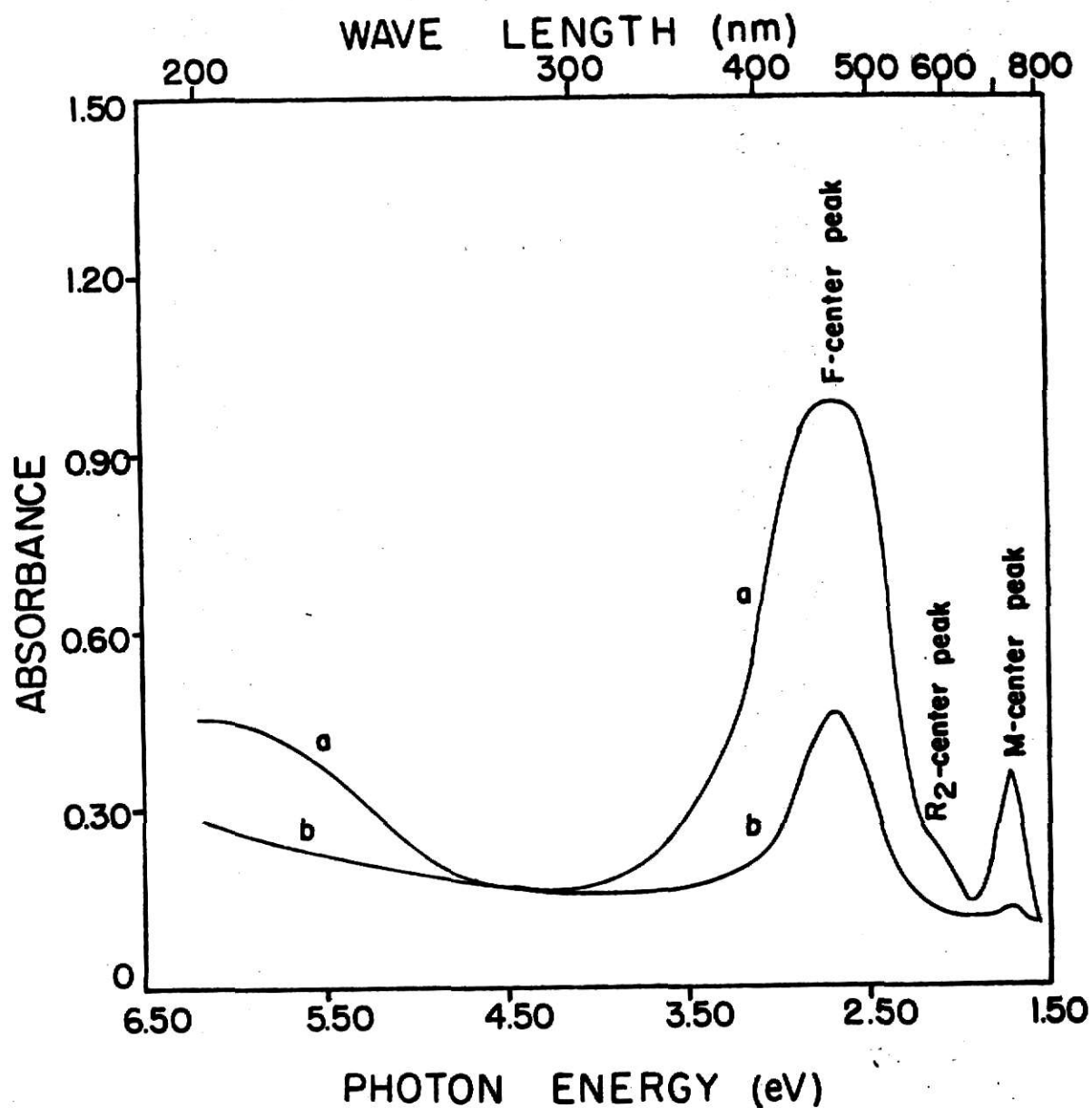


Fig. 5. Absorbance of two natural rock salt plates showing the growth of the M-,  $R_2$ -, and F-center absorption bands. (a) Dose of  $67.37 \times 10^6$  rad. (b) Dose of  $.595 \times 10^6$  rad.

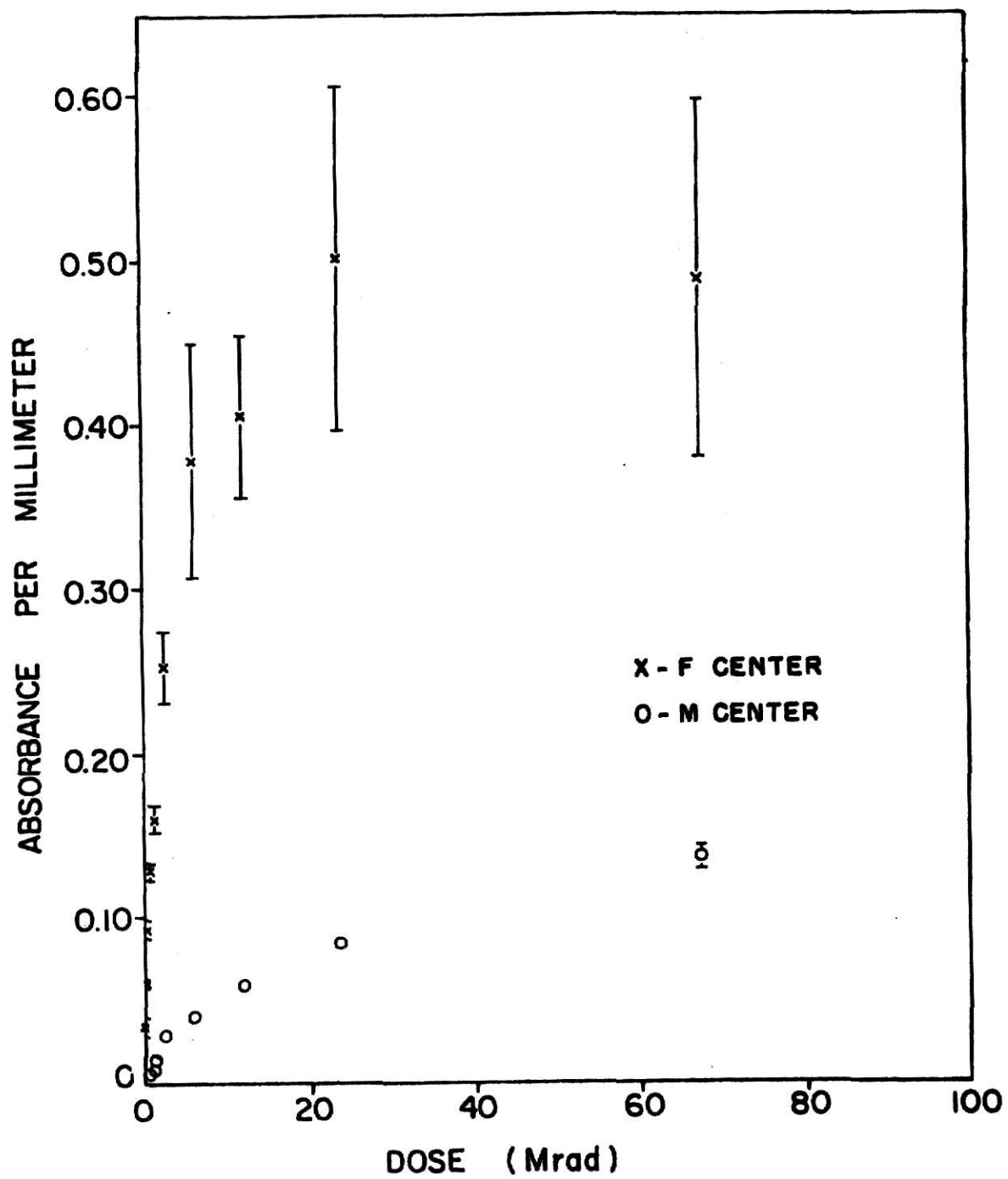


Fig. 6. F- and M-center absorbance of natural rock salt plates as a function of gamma-radiation dose.

Table I. Absorbance of the F and M Center and Thermoluminescence (peak height) at 317°C as a function of dose

Dose (Mrad)	Average Value of 465 nm Peak (absorbance/millimeter)	Average Value of 720 nm Peak (absorbance/millimeter)	Average Value of 317°C Thermoluminescent Peak (arbitrary units)
.06	.034 ± .006		
.119	.061 ± .002	.007 ± .002	.05 ± .004
.238	.094 ± .006	.009 ± .001	.066 ± .006
.595	.129 ± .005	.008 ± .002	.070 ± .009
1.19	.161 ± .008	.013 ± .003	.114 ± .013
2.38	.253 ± .022	.029 ± .002	.110 ± .014
5.95	.379 ± .072	.040 ± .005	.201 ± .022
11.90	.406 ± .050	.060 ± .005	.172 ± .016
23.51	.502 ± .105	.084 ± .003	.193 ± .019
67.37	.490 ± .110	.137 ± .010	.242 ± .022



The discrepancy in the point at which the F-center concentration starts to saturate might be explained in part by the nature of the salt being used. Their Harshaw NaCl was probably cleaved from a single crystal. The salt used to obtain the data in Fig. 5 was natural rock salt plates which may or may not have been cleaved from a single crystal. There is also the possibility of impurities in the natural rock salt. However, in the report ORNL-TM-3403 (1), "An Analysis of Energy Storage and Its Effects in the Proposed National Radioactive Waste Repository," the authors concluded from gravimetric chloride analysis that for the purpose of stored energy measurements by solution calorimetry, the samples may be considered pure water soluble NaCl. Another analysis on the rock salt from the Lyon's mine, is in Appendix A (11). Some impurities, e.g., were reported in this analysis, but none of the impurities reported could be found using neutron activation analysis (12).

It was the intent of this research to try to correlate the absorbance of the F center with energy storage in the rock salt. Lindenbaum (13) measured the energy storage of the sample irradiated to  $67.37 \times 10^6$  rad by solution calorimetry and obtained only .05 cal/g. Since the stored energy was so small for the largest dose, no further measurements were done at lower doses.

#### Thermoluminescence Versus Dose

The rock salt plates used in the absorption measurements were powdered to a particle size less than 250  $\mu$ . The powder was heated at 2°C per sec and the thermoluminescence measured. A typical glow curve of the powder is shown in Fig. 12b. There are two peaks, one at about 317°C and another at about 374°C. The 317°C peak, being significantly larger than the 374°C

peak, is used to obtain the thermoluminescent responses (see Table I).

The thermoluminescence as a function of dose has been plotted in Fig. 7.

In analysis of the plot and data, the scattering of the data is believed to be due to sampling problems, i.e., the mineral properties as well as the purity in the sense of defects causing thermoluminescence. For good thermoluminescent studies, it is known that very pure samples are required or at least with consistent impurity concentrations.

It was the intent to correlate thermoluminescence with energy storage in rock salt. However, since the measured energy storage was very small, this correlation could not be made.

#### Effect of Irradiation Temperature on F-Center Production

Natural rock salt plates were irradiated to a dose of  $1.28 \times 10^5$  rad at temperatures ranging from 23°C to 200°C. The absorption spectrum was taken and the change in the height of the 465 nm peak was measured and the results are shown in Fig. 8. The absorbance of the F center is nearly constant from 23°C to 40°C. After 40°C, the absorbance decreases in a manner similar to a negative exponential. This behavior indicates that the rate of F-center production decreases with increasing temperature.

When the rock salt plates are annealed at 400°C prior to irradiation, a new absorption peak after irradiation is observed at about 340 nm (3.65 eV). This has been ascribed to a V center. It should be noted that the peak is not observed unless the rock salt plates have been annealed at 400°C before irradiation. To illustrate the change in the 465 nm (2.67 eV), F-center absorption band, and the 340 nm (3.65 eV)  $V_I$ -center absorption band resulting from irradiation at different temperatures, the same rock salt plate has been plotted in Fig. 9 and Fig. 10. Fig. 9 is for irradiations at

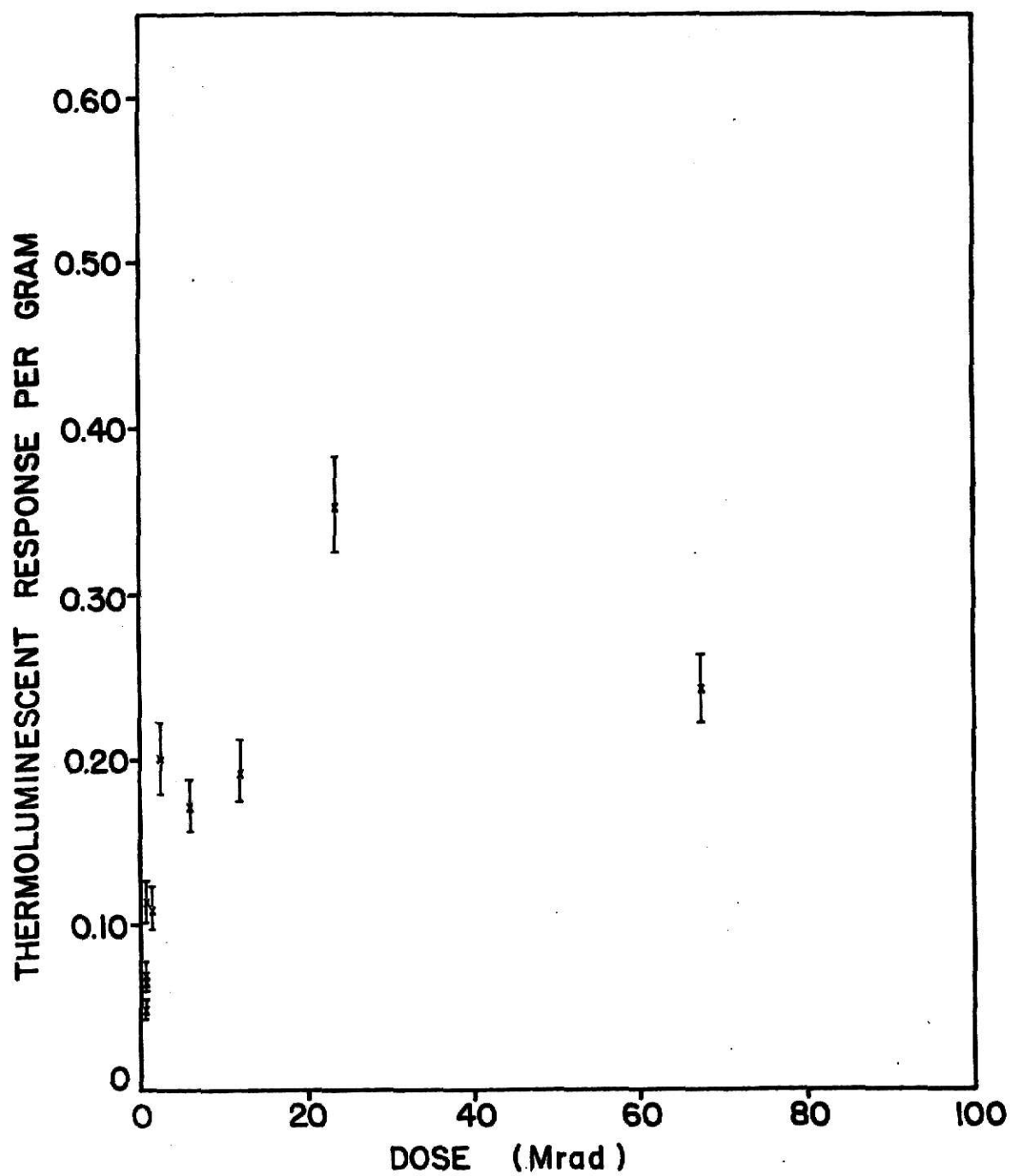


Fig. 7. Average thermoluminescent response for a  $^{60}\text{Co}$  gamma irradiated dose.

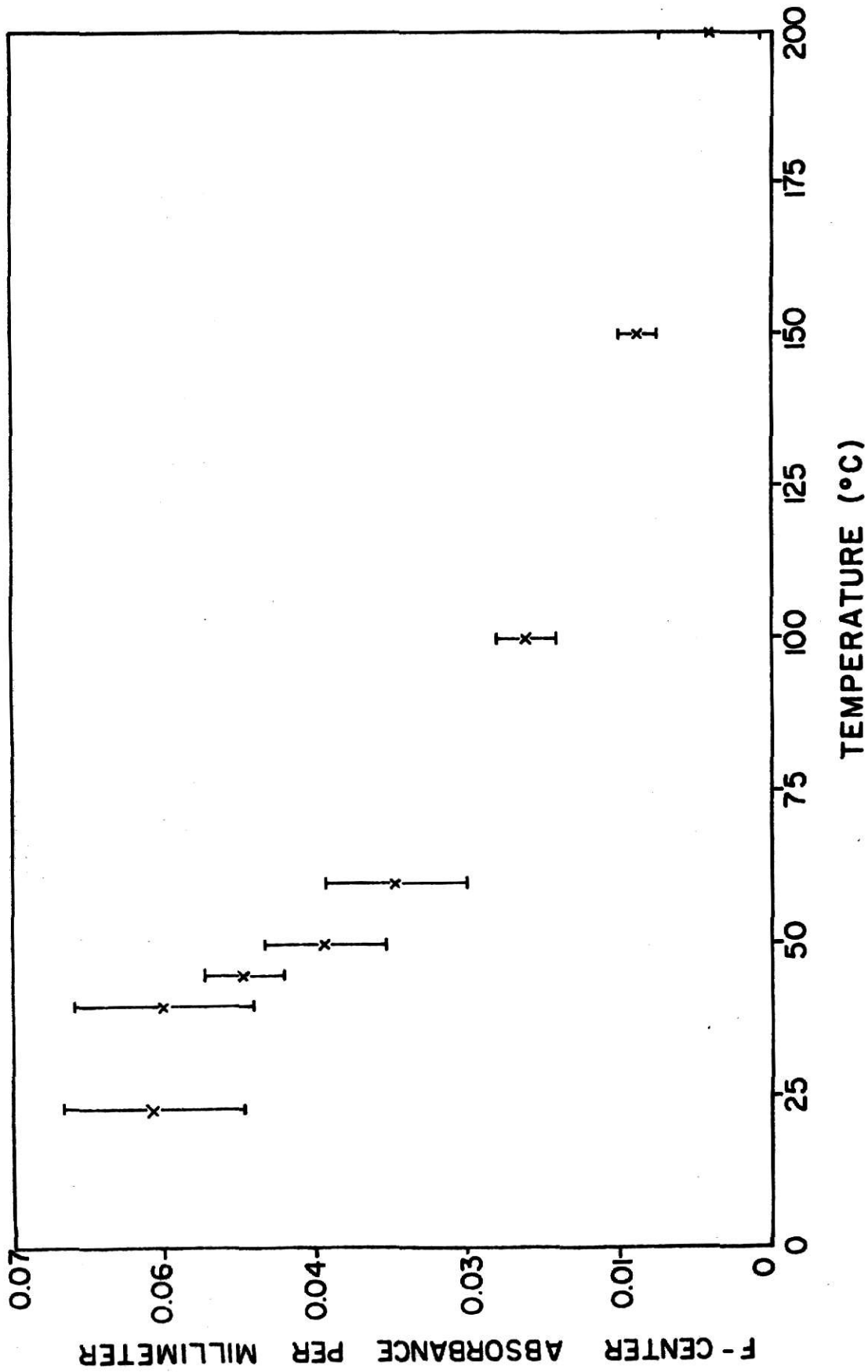


Fig. 8. F-center absorbance per millimeter thickness of natural rock salt plates as a function of irradiating temperature. The plates are  $^{60}\text{Co}$  gamma irradiated to a dose of  $1.28 \times 10^5$  rad.

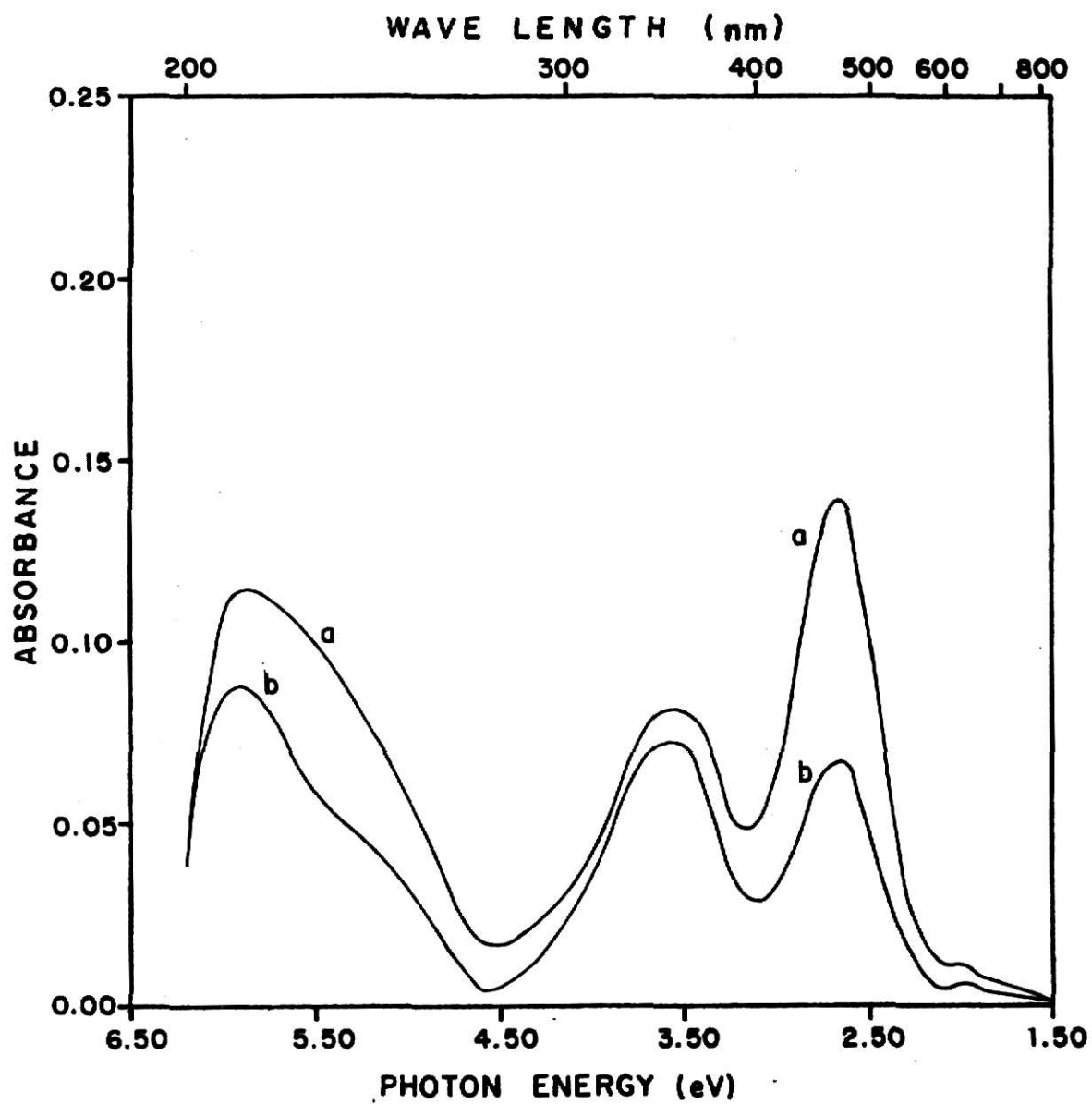


Fig. 9. Absorption spectra of a natural rock salt plate  $^{60}\text{Co}$  gamma irradiated to a dose of  $1.28 \times 10^5$  rad at (a) 23°C and (b) 60°C.

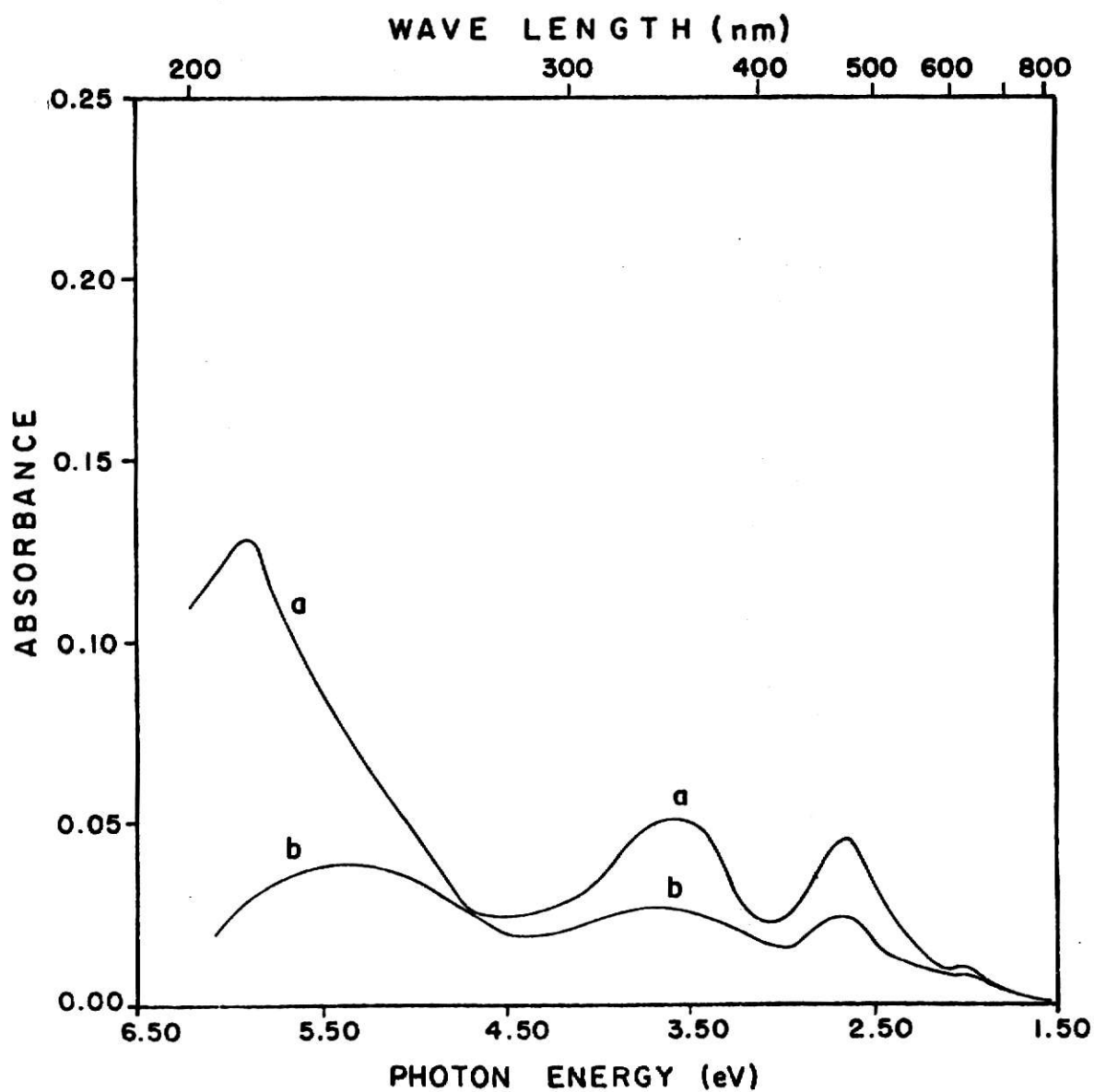


Fig. 10. Absorption spectra of a natural rock salt plate  $^{60}\text{Co}$  gamma irradiated to a dose of  $1.28 \times 10^5$  rad at (a) 100°C and (b) 200°C.

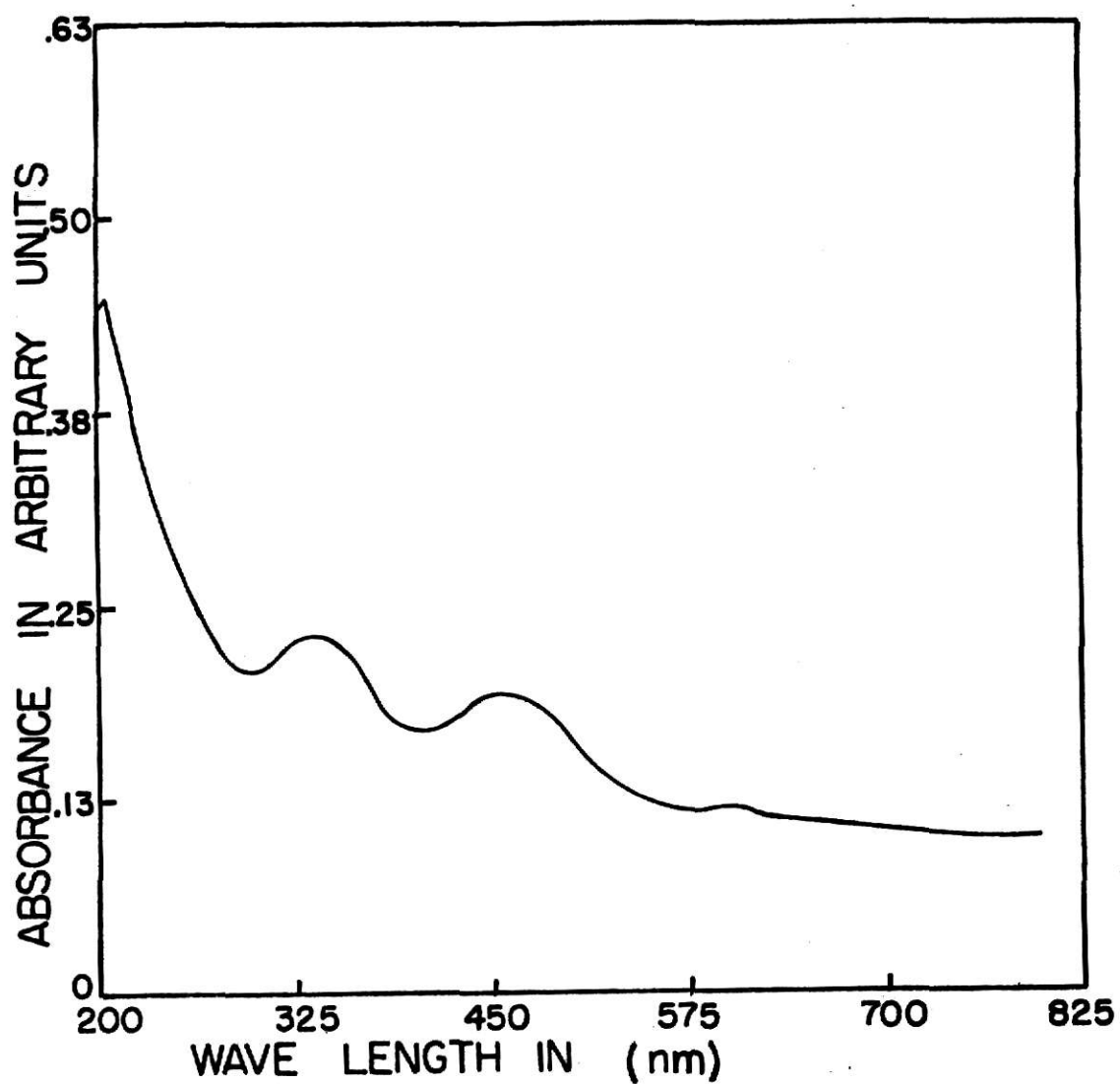


Fig. 11. A typical absorption spectrum of a natural rock salt plate  $^{60}\text{Co}$  gamma irradiated to a dose of  $1.28 \times 10^5$  rad at  $60^\circ\text{C}$ . The self absorbance of the plate has not been subtracted.

23°C and 60°C. Fig. 10 is a plot for the 100°C and 200°C irradiation. To better illustrate that the 620 nm (2 eV) peak is real in Fig. 9 and 10, an absorption spectrum of the 60°C irradiation is shown in Fig. 11. (The difference in the latter is that the background has not been subtracted.) As a result of irradiating at various temperatures, there is a general trend toward lower absorbance in the M-, F-, and  $V_1$ -center absorption bands with increasing temperature of irradiation. The absorbance in the  $V_3$  band (215 nm) also decreases with increasing temperature of irradiation except at 100°C where its absorbance is greater than at 60°C. This may be real or a consequence of the positioning of the crystal.

#### Rock Salt Coloration

Rock salt that had been irradiated to a dose of  $59 \times 10^6$  rad was heated from 100°C to 400°C. The change in color is observed at each temperature and summarized in Table II. The change in color from brown to blue is consistent with the results others have found. Seitz (6) found that additively colored NaCl containing atomically dispersed F centers, which is yellow in color, turns blue after being annealed at temperatures in the vicinity of 400°C. Seitz (6) reports that Gyulai showed that the blue coloration is obtained in additively colored NaCl. S. V. Pappu and McCarthy (7) report that a "heavily" irradiated crystal whose absorption spectrum showed F, M, R, N, and V centers has turned violet in color (as revealed under transmitted light) upon isothermal bleaching at any temperature in the range 160–200°C, and the absorbance of such a crystal at room temperature shows a single band with its peak located at about 560 nm.

This is exactly what is found when an absorption spectrum is taken of a violet piece of irradiated rock salt from the Lyon's mine, i.e., there is a single absorption band with its peak located at about 560 nm. When the salt



Table II. Rock Salt Irradiated to  $59 \times 10^6$  rad and Annealed for 5 minutes  
at each temperature for Color Analysis

Temperature in °C of the Furnace	Color of the Rock Salt
$96 \pm 2$	Brown
$146 \pm 2$	Brown
$171 \pm 2$	Brown - Later turned Gray Black
$186 \pm 2$	Dark Blue
$196 \pm 2$	Light Blue
$221 \pm 2$	Clear
$225-400 \pm 2$	Clear

is blue in color, the absorption spectrum contains a single band with its peak at 580 nm. The blue, purple, and violet colors observed in irradiated salt is attributed to the scattering and absorption of light by particles of colloidal sodium (7).

The mechanism for colloid evolution is that the F center diffuses via a vacancy mechanism and agglomerates upon heat treatment (7). Also, in irradiated salt there are additional factors such as lattice damage done during irradiation and electron-hole recombination, both of which might play a significant role in the formation of the colloids ( $C_1$  centers) (7).

In the Project Salt Vault experiment the darkest coloration of the salt is at the highest temperature and highest absorbed dose. But Kubik (14), reports that contrary to expectations, the greatest amount of energy was released from samples at 8 inches (20 cm) along the core (6 in. or 15 cm from the array hole).

Holdoway (14) gives the following explanation. It is known that defects may migrate to regions of dislocations, and thus defects resulting from radiation could become concentrated in areas where the combined effects of radiation and stress are the greatest. This would account for the greatest amount of stored energy at 6 inches (15 cm) away from the edge of the array hole, and not at the edge where possible inward relaxation reduces the total stress.

Once the blue or violet color (colloid centers) in a crystal are formed, it is very stable against heating. Holdoway (14) has found, in thermoluminescence studies of the irradiated salt from the Project Salt Vault, that the annealing of purple peak corresponds to a 350°C TL peak and the annealing of blue peak corresponds to a 400°C TL peak.

The different color arises from the size of the colloidal particle and for additively colored NaCl is summarized in Table III (3).

In rock salt irradiated in situ during the Project Salt Vault experiment, Holdoway (14) finds that the salt color varies with distance from the array hole as follows. "In the core examined, the salt nearest the array hole is blue-black in color. Further from the array hole the intensity of the blue coloration gradually decreases, the salt being royal blue at 7 inches (17.5 cm) from the array hole. The salt ranges from purple to pale purple from 9 to 18 inches (22.5-45 cm) from the array hole. No coloration is observed in these sections beyond 18 inches (52 cm) from the array hole. Small patches of purple salt occurs in the dark blue salt, but blue coloration is not observed in the purple salt" (14).

During the Project Salt Vault experiment temperatures did not exceed 200°C at the wall of the array hole, and varied from 200°C to room temperature away from it.

Table III. Coloration of NaCl by Colloidal Na<sup>+</sup>

$\lambda$ max (nm)	Particle diameter (nm)	Color by transmitted light
550-575	0-20	reddish-purple
575-600	20-40	purple
600-650	40-80	blue

†From reference 3.

When a piece of violet and blue rock salt from the Project Salt Vault with a copper constantan thermocouple cemented in it is heated, the salt turns blue and the color begins to disappear at 350°C. As the color disappears,

it is accompanied with a crackling sound. (The salt remains in one piece with no visually observable structural damage.)

### Differences in Thermoluminescent Glow Curves as the Form of the Salt is Changed

Thermoluminescent glow curves of samples in powdered form have three peaks (see Fig. 12b). There is a very small peak at  $\sim 122^{\circ}\text{C}$ . The largest peak is at  $\sim 317^{\circ}\text{C}$ . There is a shoulder at  $\sim 374^{\circ}\text{C}$ . It should be noted that these rock salt plates had not been annealed before irradiation.

Natural rock salt plates that have been irradiated for 1 hour, have five peaks, i.e., one at  $\sim 134^{\circ}\text{C}$ ,  $\sim 152^{\circ}\text{C}$ ,  $\sim 188^{\circ}\text{C}$ ,  $\sim 224^{\circ}\text{C}$ , and  $\sim 272^{\circ}\text{C}$  (see Fig. 12a). The peak at  $\sim 272^{\circ}\text{C}$  is the largest in peak height. It has a thermoluminescent response per gram of  $87 \times 10^{-6}$  A. J. Bunch and E. Pearlstein (2) have done some simple thermoluminescent studies in which crystals of NaCl (Harshaw) ( $^{60}\text{Co}$   $\gamma$ -irradiated to a dose of  $200 \times 10^5$  rad) were heated at  $5^{\circ}\text{C}$  per minute. They observed one peak at about  $272^{\circ}\text{C}$ . It should be pointed out that it is difficult to correlate peaks when different sized crystals and different reading units are used as the heat transfer characteristics are different which results in a shift of peak height to either lower or higher temperature.

Natural rock salt, sample one in crystal form and the other in powder form, are annealed at  $400^{\circ}\text{C}$  for 1 hour and then irradiated for 1 hour with  $^{60}\text{Co}$  gamma-rays. The irradiated powder has 3 peaks in its TL response (see Fig. 13a). There are peaks at  $\sim 144^{\circ}\text{C}$ ,  $\sim 218^{\circ}\text{C}$ , and  $\sim 316^{\circ}\text{C}$ . The peak at  $\sim 316^{\circ}\text{C}$  is the main peak. It has a thermoluminescent response of  $85 \times 10^{-6}$  A and corresponds to that of an unannealed crystal. The crystal irradiated at the same time for 1 hour shows one very broad peak at  $\sim 270^{\circ}\text{C}$  with a response of

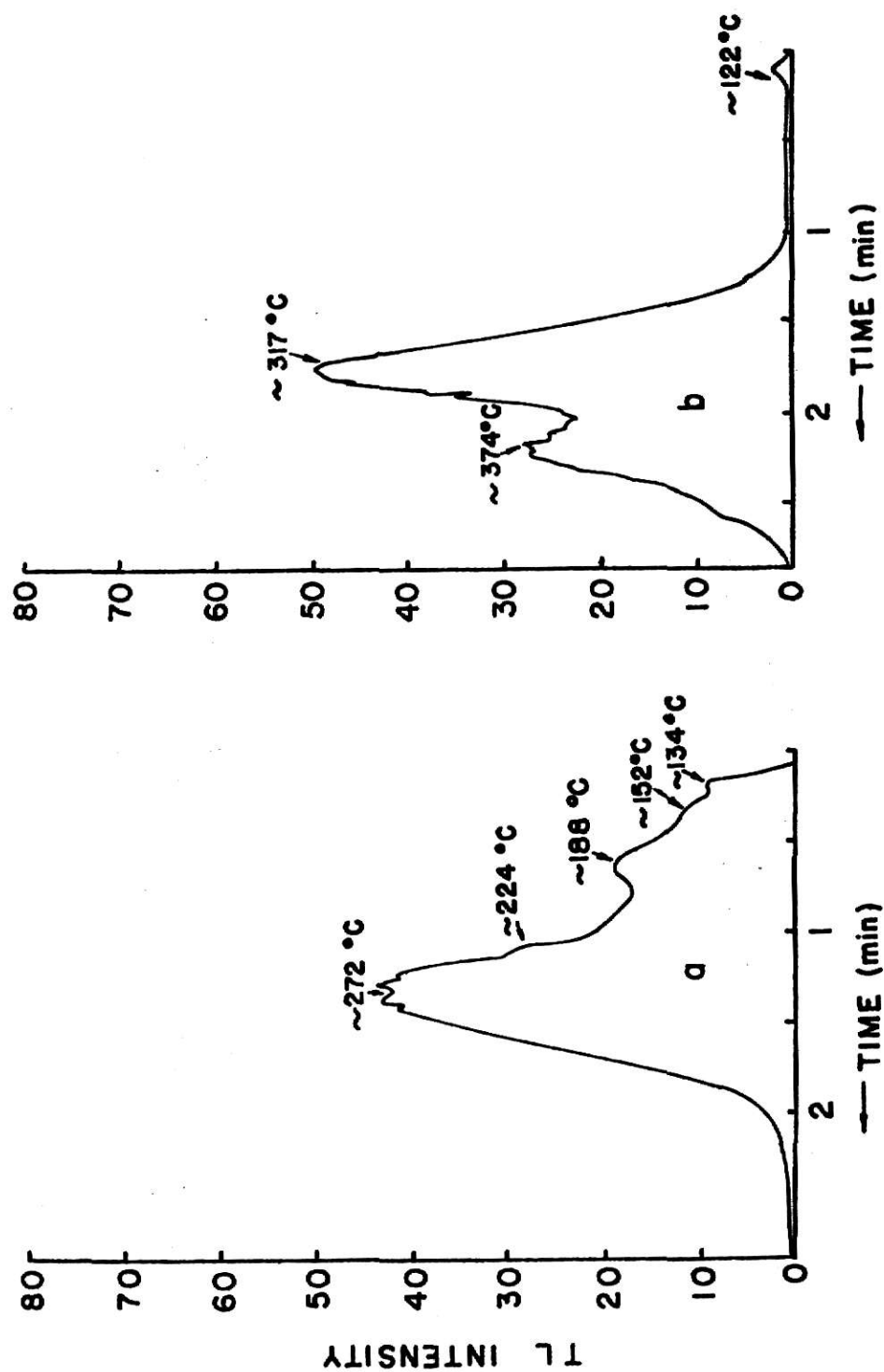


Fig. 12. Typical glow curves of  $^{60}\text{Co}$  gamma irradiated (a) rock salt plate, dose of  $1.19 \times 10^5$  rad  
(b) rock salt plate irradiated and then powdered, dose of  $67.37 \times 10^6$  rad.

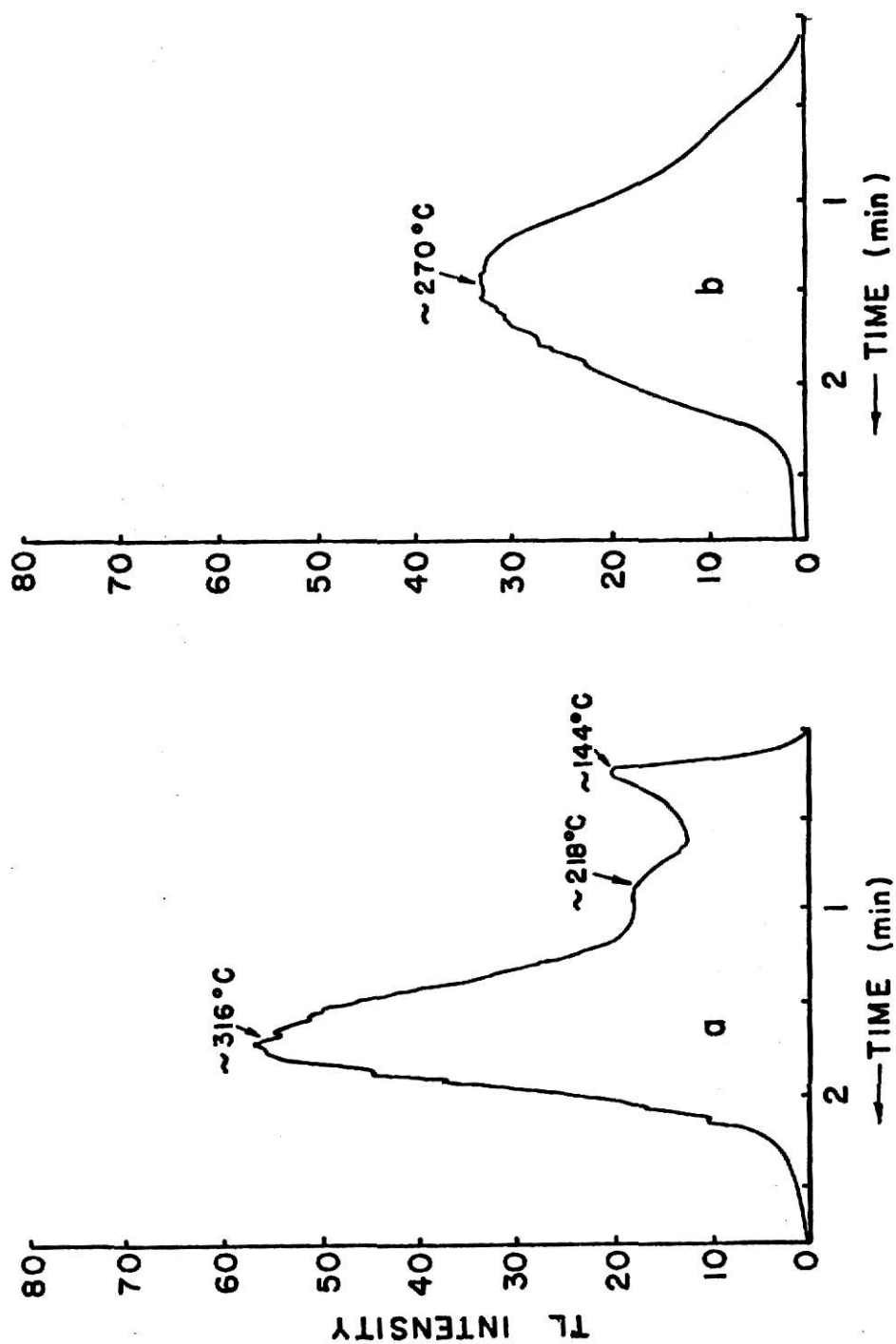


Fig. 13. Typical glow curves of  $^{60}\text{Co}$  gamma irradiated (a) rock salt powdered and then irradiated, dose of  $1.19 \times 10^5$  rad and (b) of a rock salt plate annealed and irradiated under identical conditions as the powder.

$22 \times 10^{-6}$  A (see Fig. 13b). The powder has a response approximately four times that of crystalline form. An explanation for the increased response over the crystalline form is that the powder has more surface area. But, why the powder response should seem to agree so well with that of an unannealed 1 hour irradiated crystal, this researcher has no explanation.

As previously stated, heavily irradiated rock salt turns blue when it is crushed. A glow curve of the powdered blue salt shows two peaks. The main one is at  $\sim 317^{\circ}\text{C}$  and a smaller shoulder peak occurs at  $\sim 374^{\circ}\text{C}$ .

According to the theory that the blue color is due to the colloid center formation, then the increase in temperature at which thermoluminescence occurs is as one would expect.

#### IV. CONCLUSIONS

The results of the room temperature absorbance measurements of the F center show that the F-center concentration in gamma irradiated natural rock salt from Lyons, Kansas saturates. This saturation has been observed for gamma irradiated Harshaw NaCl crystals (10). Saturation for natural rock salt occurs at a higher dose than for Harshaw NaCl crystals (10). The break in the absorption coefficient versus dose curve for natural rock salt occurs at a dose of approximately  $18 \times 10^6$  rad. The break in the absorption coefficient versus dose curve of Harshaw NaCl crystals occurs at a dose of about  $4.2 \times 10^5$  rad (10). The absorption coefficient for the onset of saturation in each curve is  $4 \text{ cm}^{-1}$  and  $12 \text{ cm}^{-1}$  respectively. The saturation concentration of F centers is lower in natural rock salt from the Lyons, Kansas mine and long irradiation times are required for saturation of the F center in natural rock salt.

If established that the growth of the M center in pure (Harshaw) NaCl crystals behaved similarly to the M-center growth in natural rock salt, then the amount of energy that natural rock salt could store would be less than for pure NaCl crystals.

Stored energy measurements were made using a solution calorimeter accurate to approximately .025 cal/g. The sample of rock salt used was irradiated to a dose of  $67.37 \times 10^6$  rad. This dose was well into the F-center saturation level and possibly into the M-center saturation level. The stored energy measurement yielded .05 cal/g (13). Stored energy of .05 cal/g is lower than the 4 cal/g that Bunch and Pearlstein (2) reported for a F-center saturation concentration of  $2 \times 10^{19}$  F centers /cm<sup>3</sup> (1). Authors of ORNL-TM 3403 (1) have reported that for doses up to  $10^{11}$  rad,



no more than 2 to 3 cal/g can be stored in natural rock salt where the dose rate was of the order of  $10^9$  rad /hr.. Rock salt irradiated to  $10^{11}$  rad could have reached or approached M-center saturation, thus accounting for the higher stored energy values.

The results of irradiating natural rock salt at different temperatures, between 23°C and 200°C, has shown that the F-center concentration at 200°C is small.

Detailed studies of the trapped hole centers (V centers) formed when rock salt crystals had been annealed for 1 hour at 400°C and then irradiated, were not made. But from the results, a couple of general trends seem worth mentioning. First, that no V centers were observed in any of the unannealed crystals. Secondly, that as irradiating temperature increases, the formation of V centers decreases as does the formation of F and M centers.

The same rock salt plates used for the F-center absorbance measurements were powdered and some simple thermoluminescent measurements made to see if the thermoluminescence would saturate. As a result of these measurements, there seemed to be a saturating trend but scattering of data points would not permit any reliable comparison. The scattering of data points was attributed to inconsistent impurity and defect concentrations in the rock salt.

Powdering irradiated rock salt and subsequent exposure to fluorescent lights of the room will cause the formation of light blue colloidal centers.

Control samples of unirradiated powdered salt show no peaks in their glow curves. When unannealed crystals are irradiated and then powdered there are three peaks in the glow curves, a very small peak at  $\sim 122^\circ\text{C}$ , a large peak occurs at  $\sim 317^\circ\text{C}$ , and a smaller shoulder peak at  $374^\circ\text{C}$ . We find that when glow curves are taken of unannealed, 1 hour irradiated rock salt

in the crystalline form there are five peaks, the largest peak occurring at  $\sim 272^{\circ}\text{C}$  and has a response per gram of  $87 \times 10^{-6}$  A. A glow curve of an annealed then subsequently 1 hour irradiated crystal shows 3 peaks, the largest occurring at  $\sim 316^{\circ}\text{C}$ . The  $316^{\circ}\text{C}$  peak has a response per gram of  $85 \times 10^{-6}$  A. A crystal (rock salt plate) annealed and irradiated at the same time as the above powder shows only one broad peak at  $\sim 272^{\circ}\text{C}$  with a response per gram of  $22 \times 10^{-6}$  A. Thus, if the response of the largest peak is used, the powdered salt has a response of approximately 3.85 times that of the crystal both annealed and irradiated under identical conditions. This seems to indicate that the thermoluminescence is a function of surface area.

## V. ACKNOWLEDGEMENTS

This research was visualized and designed by Dr. Joseph F. Merklin and Dr. Hermann J. Donnert. The writer is highly indebted to Dr. Merklin and Dr. Donnert for their guidance, instruction, and help during all phases of this work. He also appreciated their patience and humane qualities.

Sincere thanks are offered to Dr. Edward J. Zeller and Dr. G. Dreschhoff of the Departments of Physics and at the University of Kansas Geology for their discussions on the subject and stored-energy measurements by differential thermal analysis, and to Dr. S. Lindenbaum of the School of Pharmacy, University of Kansas, for his aid with solution-calorimeter measurements. Further thanks are due to Daniel Pinkham, Carey Salt Company, Hutchinson, Kansas for his chemical analysis and to Dr. N. Dean Eckhoff, Department of Nuclear Engineering, Kansas State University, for performing the neutron activation analysis.

The financial assistance given at Kansas State University by the Department of Nuclear Engineering and the U.S. Department of Defense (Office of Naval Research) through project THEMIS is gratefully acknowledged.

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## APPENDIX A

ANALYSIS OF LYONS, KANSAS ROCK SALT FROM THE  
 "PROJECT SALT VAULT" MINE

Analysis Reported (Dry Basis)

Acid Insolubles ---	0.0400%
Iron Oxide -----	0.0016%
Calcium Carbonate -	0.0000%
Calcium Sulfate ---	3.6080%
Calcium Chloride --	0.0440%
Magnesium Sulfate -	0.0000%
Magnesium Chloride-	0.0280%
Sodium Sulfate ----	0.0000%
Sodium Chloride ---	96.2784%
Moisture -----	0.0000%
Water Insolubles --	0.1390%
Sodium Chloride by EDTA -----	96.2900%

Remarks: Analyst, Dan Pinkham (11), cautions against putting too much emphasis on results of just one sample since the variability in Lyons, Kansas rock salt is fairly high. However, the results compare favorable with some others of salt taken from Lyons.

## APPENDIX B

## RELATION BETWEEN THE WAVELENGTH OF A PHOTON IN nm AND ITS ENERGY IN eV

The relation between the photon wavelength and its energy is given by the Einstein equation:

$$E = hc/\lambda$$

or,

$$\lambda = hc/E$$

where:

$E$  = the energy of the photon,

$h$  = Plank's constant =  $6.625(10^{-27})$  erg sec,

=  $4.158(10^{-15})$  eV sec

$c$  = speed of light =  $2.99(10^{10})$  cm/sec

$\lambda$  = wavelength of the photon.

If  $\lambda$  is expressed in nm, and  $E$  in eV, the constant in the Einstein relation can be written as

$$hc = 1240 \text{ nm eV} .$$

RADIATION EFFECTS ON NATURAL ROCK SALT FROM  
"PROJECT SALT VAULT," LYONS, KANSAS

by

DENNIS R. ALEXANDER

B.S., Kansas State University, 1971

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Nuclear Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1973

## ABSTRACT

The optical absorption of the F- and M- center absorption bands as well as thermoluminescent measurements, in room temperature  $^{60}\text{Co}$  gamma irradiated natural rock salt from the Lyons, Kansas Project Salt Vault experiment, were studied. The absorbance was measured for doses ranging from  $.06 \times 10^6$  to  $67.37 \times 10^6$  rad. The F-center absorbance showed a definite saturation. The M-center absorbance had not saturated at a dose of  $67.37 \times 10^6$  rad. The thermoluminescent measurements showed a trend of saturating; however, scattering of data would not allow any definite conclusions to be drawn.

Solution calorimeter measurements, on samples of salt irradiated at room temperature to a dose of  $67.37 \times 10^6$  rad, showed that the samples contained 0.05 cal/g of stored energy.

Optical absorption of the F center was also studied as a function of irradiating temperature in the range  $23^\circ\text{C}$  to  $200^\circ\text{C}$ . The absorbance was rather constant from  $23^\circ\text{C}$  to  $40^\circ\text{C}$  then fell off similar to a decaying exponential. At  $200^\circ\text{C}$  irradiating temperature, the absorbance was small.

Natural rock salt that has been irradiated from  $.06 \times 10^6$  to  $67.37 \times 10^6$  rad and then powdered will upon exposure to room fluorescent light turn blue in color. Rock salt irradiated to  $59 \times 10^6$  rad undergoes a color change as the salt is heated.

Thermoluminescent measurements revealed that the shape and number of peaks in the glow curve will change depending on the history of the rock salt.