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THE SCINTILLATION RESPONSE OF LITHIUM FLUORIDE

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PREFACE

Nomenclature and terminology used is taken from the standard radiation dosimetry references; 1. "The Theory and Practice of Scintillation Counting" by J. B. Birks,¹ and 2. "Radiation Dosimetry" by G. J. Hine and G. L. Brownell.⁹

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ABSTRACT

Lithium fluoride crystals, with TiF added to the charge, were prepared by the Bridgman-Stockbarger method. The scintillation response to photon energies between 25 and 1250 keV for these crystals and a commercially prepared LiF (Ti) crystal was studied. The response of the LiF (Ti) crystal was compared to the response of an NE109 scintillator at 1250 keV. The dose response of the LiF (Ti) crystal was evaluated over the energy range 25 to 1250 keV. The absorption and emission spectra of the LiF (Ti) crystal are discussed. A historical review precedes the discussion.

INTRODUCTION

General

This project evaluates the properties of LiF (activator) as a scintillation phosphor which might have practical applications in the direct measurement of radiation dose rates.

Scintillation detection is one of the most sensitive and reliable methods used in the measurement of radiation. Its development in the last twenty years has been the result of recent improvement in the technology of phosphors, photomultiplier tubes, and associated electronic components. Immediate application of various phosphors, e.g., NaI (Tl) in gamma spectrometry dictated the lines of early research in the 1950's and 60's.¹ This resulted in a prolific production of papers on several alkali halide phosphors exploring almost every facet of investigation possible.²

Less researched and documented were those alkali-halide crystals that did not possess properties immediately useful to the nuclear industry.^{1,3} Those that did not show immediate use or which were difficult to prepare commercially have been reinvestigated and found to exhibit properties that make them useful in newly developed dosimetry techniques. For example, LiF and CaF_2 are now used as thermoluminescent dosimeters⁴⁻⁶; and CaI_2 (europium or thallium) have resolutions as good as or better than NaI (Tl), and thus are useful in gamma spectroscopy.^{7,8}

In the past decade, the thermoluminescent properties of LiF and CaF_2 have undergone extensive investigation.⁴⁻⁶ The results of these

investigations have shown that LiF crystals exhibit certain optical and physical properties that are essential for scintillator phosphors.⁹⁻¹¹

LiF exhibits an additional extremely important property in that its response to X and gamma radiation is approximately equivalent to that of tissue.¹² This property, together with LiF's thermoluminescence, have made it an excellent passive-type dosimeter. Although LiF has many desirable properties, particularly in dose assessment, the use of LiF doped with various activators has not been investigated in detail as a scintillation phosphor. Nevertheless, theoretical concepts and portions of empirical data from previously studied inorganic phosphors are also applicable to LiF.

Project Substance and Purpose

The proposed scope of the project will include:

- A historical review of scintillation phosphors and processes.
- A review of the theoretical model for the scintillation process for alkali halide crystals, including the fundamental interactions of radiation with matter, energy transport, and color center emission.
- A study of the various methods of crystal preparation, including preparation by the Bridgman-Stockbarger method and commercially by the Czochralski method.
- An evaluation of LiF crystals with respect to energy response, tissue equivalence, and efficiency at a given energy as compared to a standard scintillation phosphor.

The project encompassed four phases. First, LiF crystals, with TlF and AgF added to the charge, were prepared using the Bridgman-Stockbarger method.¹³ Commercially obtained crystals with an activator ion, prepared by the Kyropoulos or Czochralski methods,^{14,15} were compared to those prepared by the author. In the second phase, the amount of activator ion in each crystal was determined by x-ray fluorescent and atomic spectrophotometric methods. The third phase investigated the scintillation response of the LiF (activated) crystal over the energy range 20 to 1250 keV (eff). The response of the LiF (activated) crystal was compared to an organic scintillator (NE 109) of known response at 1250 keV (eff). In the concluding phase, the absorption spectrum was measured from 200 to 700 nm. The emission spectrum was also investigated. Finally, the results were analyzed and conclusions drawn.

I. HISTORICAL REVIEW

A. Introduction

The historical review considers the basic work done on scintillation phosphors and the scintillation process in general. Its focus is specifically upon the preparation of alkali halide scintillators, their scintillation and spectral responses, and upon inorganic dose-equivalent scintillators. It will not encompass related topics such as scintillation material, nor will it include a discussion of advances in the development of photomultiplier tubes, or associated electronics.

B. Scintillation Phosphors

The first studies of the scintillation process were made by Crookes and Regener (reported in Ref. 16) in 1908. In 1919 Rutherford,¹⁶ in his historic discovery of artificial nuclear disintegrations, used a zinc sulfide phosphor screen and visually counted the visible scintillation flashes. The first attempt to count scintillation pulses electronically was reported in 1940 by Krebs¹⁷ who used a photosensitive Geiger-Muller tube arrangement. It was not until the late 1940's, with the work of Curran and Baker¹⁸ and Coltman and Marshall¹⁹ that the scintillator became a practical tool in the burgeoning nuclear industry. A major breakthrough for gamma spectroscopy occurred in 1948 when Hofstadter²⁰ reported on alkali halide phosphors and in particular, NaI (Tl), which was twice as efficient as the best organic median, anthracene. Broser and Kallmann²¹ who researched CaWO_4 , also reported on naphthalene.

One of the first articles published on LiF as a scintillation phosphor was by Farmer et al.²² in 1949. The article reported that a LiF crystal (cooled with dry ice) exposed to polonium alphas, polonium-beryllium neutrons, and to cobalt-60 gammas did scintillate, but made no comparison of its response to other scintillators. Pure LiF was reported by Watts et al.²³ in 1962 not to scintillate over the temperature range 80° to 300°K.

1. Doping Alkali-Halide Crystals

One of the major problems in growing scintillation crystals has been the doping of the host crystal with various activator ions. Practical commercial techniques for growing various alkali-halide crystals with several different activators have been reported in the early 1950's by Harshaw et al.²⁴ Owen,²⁵ and Bonanoni and Rossel.²⁶ Bonanoni used the Kyropoulos¹⁴ method for obtaining alkali iodide crystals doped with 1% Tl⁺. The Bridgman-Stockbarger¹³ method was reported by Birks¹ to yield a better crystal structure and a more uniform dispersion of the Tl activator ions. This latter method has been used in this research project to dope LiF with thallium. The Kyropoulos¹⁴ and the Czochralski¹⁵ methods of pulling crystals from a melt currently are used for the commercial preparation of many crystals.

Shamovskii et al.²⁷ reported the doping of NaI crystals with thallium in the form of Tl₂O. The concentration in his experiment was 0.04 to 0.05 wt% thallium in the crystal. However, subsequent investigation revealed that in a usable portion of the rough crystal the average wt% thallium was only 0.01. Harshaw et al.²⁴ and Birks¹

reported similar distribution results, 0.1 to 0.4 mole%, with 0.1 mole% in the usable crystals. Harshaw reported that the response of NaI (Tl) was constant for dopant concentrations of 0.1 to 0.4 mole%.

A method of doping alkali halide crystals with various activators by a technique similar to that of drifting lithium into germanium crystals was reported by Lushchik in 1957.^{28,29} The activator concentration was determined at varying distances in the crystal by a method proposed by F. D. Klement.³⁰ Lushchik³¹ used both the doping technique and the method proposed by Klement for determining activator concentrations in preparing alkali halides with mercury like ion activators (Ga^+ , Ge^{2+} , In^+ , Sn^{2+} , Tl^+ , Pb^{2+}). It was reported by Lushchik that Tl^+ ions diffused by means of a vacancy mechanism. The Tl^+ or similar activator ions in the host displace the cations in the crystal lattice.

Van Sciver³² gives an excellent review of work in the United States, both currently in progress and previously reported, on alkali halide phosphors.

In 1963, Zazubovich³³ prepared KCl doped with Tl^+ ions by the Kyropoulos method. Other activated alkali halides, e.g. KCl (In), and KCl (Sn), were prepared by the Stockbarger method. The amount of activator for this experiment³³ varied between 0.001 and 0.01 mole%. At this time, Kuketaev³⁴ also prepared single crystals of NaCl (Ag, 0.03 to 0.5 mole%), KCl (Ag, 0.02 mole%), RbCl (Ag, 0.03 mole%), and others by the Kyropoulos method. Gwin and Murray³⁵ reported on the response of CsI (Tl). The Tl concentration was reported for this particular experiment³⁵ to be 0.046 mole%. The effect of Tl

concentration on the luminescence of various phosphors compared closely with the theoretical calculations of Murray and Meyer.³⁶ In 1961, Robertson and Lynch³⁷ reported on the response of the alkali halides KI (Tl), LiI (Eu) and CsBr (Tl). This work did not include sample preparation or concentrations of the various activator ions.

2. Alkali-Halide Crystals Doped with Large Cations

Hofstadter et al.⁸ and Van Sciver⁷ reported on the difficulty of growing CaI_2 with an Eu^{3+} and Tl^+ activator ions. The problem with the growth of the crystal structure CaI_2 was accentuated by the dislocation and distortion caused by the introduction of Eu^{3+} or Tl^+ ions. CaI_2 has a hexagonal crystal structure with pronounced basal cleavage, which is further stressed by the larger Tl ions. The doping of CaF_2 , which has a cubic structure with large cations (e.g., Sm^{3+} , Dy^{3+}) having ionic radii of approximately 1.0 Å, was reported by Voron'ko³⁸ in 1965. The Sm^{3+} ion was added as Sm_2O_3 or SmF_3 . Belyaev et al.³⁹ reported a higher intensity luminescence with addition of uranium (VI) nitrate to LiF. In both cases, the experimenter indicated that there was improvement in crystal structure if the starting material was first heated to several hundred degrees centigrade for several hours. After the crystals had gone through the melt phase, a prolonged annealing process (24 to 48 hr) resulted in excellent crystal structure and uniform dopant. In 1963, Alekseeva⁴⁰ made detailed studies of LiF activated with uranyl, copper, magnesium and iron salts. Grube and Schwarz⁴¹ reported on the thermoluminescent and radioluminescent response of LiF activated by Mg^{2+} and Ca^{2+} ions. The response

was reported in relative units, and no comparison was made of the response of these crystals to other known scintillators. In 1972, Iso-Met Corporation * reported⁴² difficulty in introducing Tl^{+} ion (ionic radii 1.40 Å) into the LiF melt for the crystals made for this author.

C. Air and Dose Equivalent Scintillators

Very few papers have been written on dose or air equivalent scintillators.[†] Breitling⁴³ mixed various proportions of phenanthren and chlorophenanthren to obtain an air-equivalent response for photon energies from 15 to 150 keV. Theoretically, the mixture Breitling used should have had a reasonable air-equivalent response to energies of several MeV. He based his initial proportions on values^{**} for effective $\bar{z}_{eff}$ of various compounds as derived by Hine.⁴⁴ Both Breitling and Hine reported the need for caution when using $\bar{z}_{eff}$ values for determining the percent of each component needed for an air-equivalent phosphor. It was determined by Breitling that for low energies the intrinsic efficiencies of the phosphors change, and values for $\bar{z}_{eff}$ are obtained by use of empirical data.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

†Air and dose equivalence refers to a material whose energy absorption response to radiation is similar to air and tissue, respectively.

**The effective atomic number of a material.

Ittner and Ter-Pogossian⁴⁵ obtained air-equivalent scintillators over limited energy ranges by sandwiching CaWO_4 with an organic phosphor, naphthalene or anthracene. The energy response was reported to be air equivalent down to photon energies of 80 keV. However, the sensitivity was on the order of 60 R/hr. Cole *et al.*⁴⁶ built a scintillator (AN/PDR-18) using a system similar to that reported by Ittner and Ter-Pogossian.⁴⁵ The energy response was similar to that of Ittner and Ter-Pogossian, and had a useful range of 0.05 to 500 R/hr.

In 1957, Belcher and Geslinger⁴⁷ used finely powdered ZnS (Ag) in a plastic matrix, thus improving both energy response and sensitivity. The energy response was air equivalent from 30 keV to 1.5 MeV, and the sensitivity was similar to standard G.M. Survey instruments. In 1969, Vershinina *et al.*⁴⁸ reported similar results. Kolb and Lauterback⁴⁹ reported in 1972 on the development of a ZnS (Ag) plastic matrix scintillation phosphor with an energy response equivalent to air from 20 keV to 2 MeV. The detector volume was given as 330 cm³.

Takeuchi *et al.*⁵⁰ described the use of $\bar{z}_{\text{eff}}$ values to determine phosphors that would measure the dose to tissue in units of rads. The report indicated that the best $\bar{z}_{\text{eff}}$ value was between 12 and 20. It is noted, however, that $\bar{z}_{\text{eff}}$ values previously reported⁹ for tissue, muscle, or skin did not exceed 7.4. However, bone had a reported value of approximately 13.8. The reported difference in the values of $\bar{z}_{\text{eff}}$ is an apparent conflict that must be evaluated and resolved. If the values of $\bar{z}_{\text{eff}}$ determined by Takeuchi *et al.* are correct, then CaF_2 (Eu) with a $\bar{z}_{\text{eff}}$ of approximately 13 will make an excellent

dose-equivalent scintillation phosphor. It is noted that $\bar{z}_{\text{eff}}$ for LiF has been calculated^{10,11} to be approximately 8.1, and thus more closely approaches the more frequently reported⁹ 7.4 $\bar{z}_{\text{eff}}$ of tissue. Therefore, the response of LiF to ionizing radiation should approximate the response of tissue.

D. Scintillation Theory

In 1956, Ramm⁵¹ presented a general review of the theory of basic scintillation and the scintillation detection process. The general formula for the determination of scintillator response to electromagnetic radiation was given as

$$P = E \mu_a \eta g / h\nu \quad (1)$$

where

P = the number of photons produced in the cathode,

E = the energy of the radiation,

μ_a = the absorption coefficient of the detector,

η = the intrinsic efficiency of the particular phosphor,

g = the optical efficiency,

$h\nu$ = the energy of photons produced in the crystal.

The general response equation was quantified for dose measurement as

$$I = B d \frac{1 - e^{-ud}}{ud} \left[\tau \eta(E) E + \int_0^{\epsilon_{\text{max}}} \epsilon \times f(\epsilon, E) \eta(\epsilon) d\epsilon + K \eta(E) (E - 2mc^2) \right] \quad (2)$$

where

I = the light intensity produced by the phosphor at the photocathode,

B = a conversion factor,

$\frac{d(1 - e^{-ud})}{ud}$ = the attenuation term,

$\tau\eta(E)E$ = the photoelectric term,

$n \int_0^{\epsilon_{\max}} \epsilon f(\epsilon, E) d\epsilon$ = the true Compton term

$\epsilon\eta(\epsilon)$ = quantity proportional to the light output of the Compton electrons

$k\eta(E)(E - 2mc^2)$ = the pair production term,

μ = the attenuation coefficient,

η = the intrinsic efficiency of the scintillator,

d = the thickness of the crystal.

Equation (2) was applied by the author to calculate the relative response of LiF crystal phosphors as a function of photon energy. The relative dose response to radiation was then calculated with the assumption that all other parameters were known (see Appendix A).

The equations by Ramm agreed with the treatment by Birks,¹ Brietling,⁴³ and Carr and Hine,⁵² but did not substantiate the work done several years earlier by Taylor *et al.*⁵³ In 1964, Price⁵⁴ presented an account on scintillation similar to that of Ramm. The same year, Birks¹ published his second comprehensive text on the scintillation process. Portions of his text describe a model for activated alkali-halide phosphors which proposed the formation of

electron-hole pairs and then excitons (bound electron-hole pairs) by the process of ionization. The ionization described is caused by the interaction of photons with the crystal by the mechanisms of Compton scattering, photoelectric effect, and pair production. He hypothesized that electrons or excitons may move from the conduction band of the crystal phosphor to one of three types of centers formed by impurities or crystal defects in the host lattice (see Fig. 1). The centers described by Birks are:

- The luminescent center in which the transition accompanied by photoemission is from the excited state to the ground state.
- A quenching state that results in thermal dissipation without photoemission.
- Traps that result in radiationless transitions.

Williams⁵⁵ proposed a similar model: i.e., (1) the production of an electron-hole pair; (2) recombination to form excitons; (3) capture by color centers, e.g., Tl impurities; and (4) activation to the Tl, $^3P_1^0$ level from the ground state and decay with photonemission. The absorption process, based on the Frank Condon principle, involved a transition of the Tl⁺ ion from the ground 1S_0 state to the excited states. The energy transitions and spectra were also described in work by Lushchik^{51,56} in 1960 and later by Kukelaev³⁴ in 1968. The same basic model was reviewed and discussed by Garlick,⁵⁷ Ladu et al.⁵⁸ and Katz and Kobetich.⁵⁹ Other related topics such as the electronic structure of various centers (except impurity centers) as well as additional discussion of other aspects of scintillation theory

Fig. 1. A solid-state model of impurity centers on an activated crystal phosphor.

are available in Refs. 60-65. The qualification of Birks'¹ model and comments by Ramn,⁵¹ along with other theoretical considerations, are presented in Appendix F.

E. Summary

Numerous reports and publications have described both the theory of scintillation response and experimental results concerning various alkali-halide phosphors (activated and pure). Fewer articles have been published on the response of LiF (activated) as a scintillator. A single 15-year-old report was located on LiF (AgCl).⁶⁶ Since then, only a sparse number of articles have made reference to the possibility that LiF (activated) scintillates.

There are now several works in the journals on dose- or air-equivalent scintillators. There is evidence that it is difficult to dope LiF or similar crystals with large cations such as Tl^+ ions or Sm^{3+} .

The literature review conducted by this author supports the contention that LiF (activator) should be investigated as a scintillator.

II. EXPERIMENTAL MATERIALS AND METHODS

A. Materials

The following three types of LiF were used in crystal preparation:

- Optical grade LiF purchased from Isomet Corporation (1972). No purity analysis was provided except that all LiF used had an initial purity of 99%. No independent analysis of the LiF was made prior to crystal growth.
- Ultrapure LiF obtained from Toy¹¹ for crystals 6 and 7. The chemical analysis indicated no detectable metallic impurities (LLL spectrochemical analysis report ss0716, plates 3045 and 3047, Feb. 7, 1973).
- Lithium fluoride crystal boules purchased from Isomet Corporation. For specifications, see Table 4 and for analytical data, see Appendix C.

The remaining chemicals, all from Laboratory stock, were analytical grade, and consisted of the following:

- Absolute ethanol (Commercial Solvents Corporation).
- Hydrochloric acid (Malinkrodt Chemical Works).
- Acetone (Malinkrodt Chemical Works).
- Silver fluoride (K & K Laboratories, Lot 409851).
- Thallium chloride (K & K Laboratories, Lot 24628).

B. Methods

1. General

The methodology of single-component crystal growth is basically a controlled growth by freezing. Theoretically, single-component

systems by definition exclude all impurities either by deliberate addition, e.g. activator ions, or by improper cleaning and purifying of the initial material or crucible. However, almost all crystalline material does contain impurities, with the typical degree of contamination being less than one to three parts per million in concentration. If the impurity concentration is so small that a diffusion process involving the impurities is insignificant, the host crystal may be considered as a single component crystal. In this case the rate of formation of such a crystal should be quite rapid, and the crystal formed be of high purity with a uniform dispersion of the activator ion.

Two general methods are used for the growth of large uniform crystals for use as scintillation phosphors. The first method (Bridgman-Stockbarger) is the production of a nucleation on a single solid-liquid interface using a temperature gradient as shown in Fig. 2.

The second method (Czochralski) involves controlled pulling of the crystal from a melt as described in Fig. 3.

2. Crystal Growth by the Bridgman-Stockbarger Method (Crystals 1 through 7)

Figure 4 shows the crucible used by the author to grow LiF crystals by the Bridgman-Stockbarger method. It is a conical section of high-purity nickel with a converging tip welded to a nickel-alloy vacuum extension. The volume of the tip of the nickel crucible is small enough so that as the liquid phase was supercooled at the tip, only one nucleus of LiF should be formed. If more than one nucleus formed, a polycrystal would generally result.

Fig. 2. Temperature gradient of a furnace used for crystal preparation by the Bridgman-Stockbarger method.

Fig. 3. The Czochralski method of crystal preparation.

Fig. 4. The crucible used to prepare crystals 1 through 7 by the Bridgman-Stockbarger method.

Before each run, the crucible was placed for 10 min in an ultrasonic cleaner, using 2N HCl as a cleaning solution, followed by rinsing with acetone and ethyl alcohol. A portable sandblaster was used to polish the crucible internally and externally with 100- and 600-grit SiC. After being cleaned with high-pressure air and rinsed with acetone, the crucible was again ultrasonically cleaned, first with acetone and then with ethyl alcohol as cleaning solutions. After a final rinsing with absolute ethanol, the crucible was dried with dry He gas and baked dry at 200°C in a crucible furnace for several minutes. The system then was evacuated and held under vacuum for 2 hr at 200°C before the charge was placed in the crucible.

The LiF, for crystals (1 through 5) (see Table 1), was cleaned in absolute ethanol by successive washing and decanting. The LiF was dried by passing He gas over it and by placing it in a vacuum oven at 120°C for 24 hr. The LiF was cooled in dry air, and then placed in a container purged with dry He gas. The LiF was weighed at 22°C on a Mettler balance (see Table 1), the TlCl dopant was added, and the charge was placed in the crucible. Drying precautions were taken to

Table 1. Crucible charge and pressure for preparation of crystals 1 through 5.

Crystal No.	Wt LiF (g $\pm$ 1 mg)	Wt TlCl (g $\pm$ 1 mg)	Mole% Tl	He pressure (psia)
1	10.1605	0.0983	0.00115	0.5
2	10.8351	0.1003	0.0010	2.0
3	10.9500	0.1006	0.00099	5.0
4	10.8835	0.0985	0.00098	7.0
5	10.8670	0.1015	0.0010	14.7

minimize the reaction $\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH}$. (For weights of material used, see Table 1.) The melting point of TlCl is 430°C and the boiling point is 720°C which is below the 842°C melting temperature of LiF . Various He pressures (see Table 1) were used to observe what effects minor pressure changes would have on crystal growth.

For crystals 6 and 7, the starting material was ultrapure LiF and the dopant Ag^+ ion was added after weighing (see Table 2). The Ag^+ ion was added as AgF , whose boiling point is also below that of LiF . Note that the AgF (bright yellow) had previously been exposed to air, causing the AgF to be coated in a black oxide layer that had to be removed. The AgF was added as a single mass at the bottom of the crucible. The weight of the dopant was based on work previously reported¹⁰ for NaI (Tl) and LiF (Ag).

Table 2. Crucible charge and pressure for preparation of crystals 6 and 7.

Crystal No.	Wt LiF ($g \pm 1 \text{ mg}$)	Wt AgF ($g \pm 1 \text{ mg}$)	Mole% Ag	He pressure (psia)
6	11.0600	0.0600	0.0011	0.5
7	10.8029	0.0100	0.00019	0.5
Equivalent mole% (ppm)				
6		1100		
7		190		

The furnace (Fig. 5) was raised about the crucible at 3.8 mm/hr through two isothermal regions with a gradient between them. This permitted annealing of the crystal after growth while minimizing the introduction of thermal strain. The furnace (Fig. 5) had an independent temperature control for each heating element. Each element was

Fig. 5. Furnace used for the preparation of crystals 1 through 7.

separated by thermal insulation. The temperature controls were set at 890°C and 750°C. Before starting the drive mechanism, the charged crucible was evacuated and backfilled two to three times with ultrapure dry He. The system was then evacuated and dried at 200°C for 24 hr. Next, the system was backflushed with He and evacuated, and finally backfilled with He to approximately 0.5 psia. The system also was backfilled with He at various pressures when attempts were made to dope the crystal with Tl ions (see Table 1). Temperature control was provided by Digiset and Wheelco thermal controllers using chrome-

Table 3. Crystal furnace temperature gradient.

Distance (in. from base)	Furnace temp (°C)
17	884
16	869
15	844
14	839
13	829
12	815
11	799
10	786

alumel thermocouples for each temperature zone. The temperature gradient in the furnace cavity was obtained by inserting a chrome-alumel thermocouple from the base of the furnace and measuring the output with a *Leads and Northrup Model 8691* millivolt potentiometer. The temperature settings used to obtain the gradient given¹¹ in Table 3 were 890°C (Digiset) and 750°C (Wheelco).

The crucible and extension were removed after each crystal had been annealed for approximately 12 hr. Next, each single crystal was removed from the crucible. Some crystals were damaged or severely cracked while being removed due to sticking caused by impurities in the crucible or charge. In some cases, a small ridge of LiF formed above the main melt because of a narrow band of discontinuity on the

crucible surface at the weld. The ridge had to be removed with a reaming tool before some crystals could be removed.

Crystal 1 was removed easily from the crucible. No apparent areas of impurity were noted. The crystal was solid, with one area exhibiting different orientation and with one center occlusion. Crystal 2 was a perfect crystal with a slight oily feeling that may have been due to some thallium adhering to the surface. Crystal 3 had one large center occlusion with several large gas bubbles on the sides. The probable cause of the bubbles was trapped He gas. This type of defect was not evident in any other crystal. Crystal 4 had one small gas occlusion oriented axially through its center and a flower-pot-shaped dispersion of black material also in its center. The material was not identified spectrographically, and could have been masked by the LiF in x-ray fluorescent analysis. Crystal 5 was similar to crystal 4 with the same analytical results. Crystal 6 adhered to the side of the crucible and, when removed, developed splinter planes although the crystal was not polycrystalline in nature. No occlusions were noted in crystal 6. Crystal 7 was similar in appearance to crystal 2.

The removed crystals were cut with a diamond saw and hand-polished on one surface. The cutting operation required cooling and lubrication and positive clamping at each end of the cut to reduce thermal and sheer strain. The individual cut crystals are shown in Fig. 6.

(a) Spectrochemical Analysis—The crystals were analyzed by emission spectrography. Samples were obtained from a homogeneous mixture of top and bottom sections of the melt. A sample portion of

Fig. 6. Crystals 1 through 7 prepared by the author.

the mixture was weighed, and the results were compared with a standard LiF plate. The analysis was performed on a 3.4-m Ebert Emission Spectrograph. The results of the analysis, including the starting material for crystals 6 and 7 (Sample A), are given in Appendix C, Table C-1.

(b) X-Ray Fluorescent Analysis—The seven crystals were placed in an x-ray fluorescence spectrometer (see Fig. 7). The results were negative, less than 3 ppm for Tl ion and less than 3 ppm for Ag ions. The exciting source, i.e., ^{241}Am , was placed on a right cylindrical disk that was shielded from the detector. The secondary fluorescent x rays of the crystal material were measured with an Si(Li) detector and a ND4420 data acquisition system. The characteristic K_α , K_β , L energies were then compared to known energies. An impurity ion concentration greater than 10 ppm is required to permit an observable scintillation response. Since the concentrations of Tl^+ or Ag^+ were less than 3 ppm, there should be no significant effect of these ions on the scintillation response.

3. Czochralski Techniques and Analysis (Crystals 8 through 11)

The problem of stuck crystals and physical constraints encountered in the Bridgman-Stockbarger method were avoided by pulling the crystal from the melt using the Czochralski technique (see Fig. 4). Crystals 8, 9, 10, and 11 shown in Fig. 8 were prepared by Isomet Corporation using this technique. They were to be made to the geometrical criteria and dopant concentration specified by the author. However, the analysis of these crystals, discussed later in this section,

Fig. 7. Block diagram of x-ray fluorescence analysis system.

Fig. 8. Commercial crystals 8 through 11 prepared by Isomet Corporation.

indicated that neither the Ti^{+} dopant nor the Ag^{+} dopant requested were present. Varying amounts of titanium ion were detected.

Several criteria must be optimized using this technique to insure clean, high-quality crystals. The crystals must have a congruent melt without decomposition, and should not be reactive with the crucible or atmosphere used. The pulling rate and thermal gradients should be such that single-crystal material can be formed.

The crystals were cut at the Lawrence Livermore Laboratory with a diamond saw. A 1-cm-thick section was obtained from the center of the boule and polished. The cut crystals are shown in Fig. 8. Crystal 8 had a slight brownish tint due most likely to the titanium, as indicated in the analysis. The other three were colorless pure LiF, with no Ag or Ti detected.

The x-ray fluorescence and emission spectrographic analyses made on the commercially prepared crystals indicate no dopant. The material specifications and crystal orientation are given in Table 4 and the analysis in Appendix C, Table C-2. No further research was conducted using crystals 9, 10 and 11.

Table 4. Geometric and dopant criteria for crystals 8 through 11 prepared by Isomet Corporation.

Crystal No.	Dopant concentration	Dopant added as	Orientation
8	1-10 ppm Ti	$0.01gTi_2O_3/100gLiF$	100
9	25 ppm Ag	$AgNO_3$	100
10	75 ppm Ag	$AgNO_3$	100
11	125 ppm Ag	$AgNO_3$	100

4. Crystal Scintillation Response Measurement to Different Photon Energies

(a) Equipment—The electronic equipment used to measure the response of the LiF (Ti) crystal (8) to various photon energies included:

- A photomultiplier (PM) tube.
- A Power Design, Model 1556A, 10-6000 V, 20 mA H.V. precision d.c. power supply.
- A low-voltage supply, LLL-designed LE 13849 powered bin.
- An LLL preamplifier, LE 13558-1, charge-sensitive, low-gain, negative-input, positive-output type.
- An LLL-design, LE 13222-1, (Hatch) amplifier.
- A Nuclear Data 2200 pulse-height analyzer.
- A Franklin, Model C122OD, digital printer as output from the ND2200.
- Paper punch tape as a primary method of data storage.
- A Tektronix Model 561 oscilloscope to monitor amplifier output.
- An LLL-designed light-tight PM tube and crystal housing.
- A PDP 11/20 digital computer.
- A Calcomp 565 plotter and high-speed Dec Writer.

The PM tube used was an EMI 9635QB, 2-in., end-on type with a SiKCs photocathode. The fused silica PM tube window had a useful spectral range from approximately 165 to 650 nm. The fused silica has a lower concentration of ^{40}K than typical glass windows have. The lower ^{40}K concentration in the silica window results in a lower background signal from the PM tube. Figure 9 is a reproduction from an EMI PM tube catalog⁶⁷ of the spectral response of a 9635QB PM tube.

Fig. 9. The spectral response of 9635B and 9635QB EMI PM tubes.

The LLL-designed light-tight PM tube and crystal housing was designed for easy assembly and removal of the crystal and the PM tube. A built-in shutter was used to optically seal the PM tube and crystal from the radioactive source holder. This feature allowed for easy changing of sources without having the delay of a light-affected PM tube. The housing is described in Fig. 10. Figure 11 is a block diagram of the detector, data acquisition, data transfer, and data reduction system.

(b) Scintillation Measurement—Selected sections of each crystal, cut and polished as described in Sections II.B.2 and II.B.3, were optically coupled to an EMI 9635QB tube and placed in a light-tight housing. The small-diameter crystals (1 through 7) were each held in place by optical coupling grease. The large LiF (Ti) crystal, i.e., crystal 8, was supported by a ring housing that fit into an opening above the shutter mechanism. Since procedural changes were limited to crystal mounting, only the specific procedure used for crystal 8 will hereafter be described. The electronics equipment was connected as shown in Fig. 11. The high voltage for the PM tube was varied between 800 and 1300 V. An optimum signal to noise ratio was obtained by this method. The H.V. setting was 960 V.

The Hatch amplifier was set to give the best signal pulse shape and pulse amplitude (8 to 10 V) for the ND 2200 ADC. Pulse shape settings were 0.2 μ sec for both differentiation and integration of the preamplifier signal. A baseline restore mode was used to obtain a unipolar 8-10 V signal pulse for the ADC.

Fig. 10. Diagram of PM tube and crystal housing.

Fig. 11. Block diagram of data acquisition and data reduction systems for the response measurement of LiF crystals.

The ADC zero-fine adjust was set for maximum signal output and not for a linear energy response through the zero channel. This was due to the apparent low conversion efficiency of the crystal output. All other settings of the ND 2200 were otherwise in a normal operational mode.

The nuclides used, ^{60}Co (1.25-MeV eff.), ^{54}Mn (0.835 MeV), ^{137}Cs (0.662 MeV), ^{203}Hg (0.279 MeV), ^{109}Cd (0.022 and 0.088 MeV), and ^{241}Am (0.017 and 0.060 MeV), were placed on a holding fixture 5 cm below the LiF crystal. The shutter was in the closed position while each source was positioned and opened during counting. Each source was covered with a 1.2-mm aluminum beta shield.

Four or more spectra of 100 or 1000 sec were taken for each nuclide. Background spectra were obtained for 10,000 sec. Representative photographs of the data were taken from the display scope (see Section III.A for results). Each spectrum was recorded on Tally punch tape for subsequent data reduction on the PDP 11/20 at a later time. For immediate comparison, the results were also printed out by a Franklin Printer.

The crystal and PM tube were removed from the housing in a dark room after all response data of LiF (Ti) were obtained. A ring spacer, equivalent to the thickness of the LiF (Ti) crystal, was placed in the PM tube housing and the housing was resealed.

The response of the PM tube to the radioactive sources was obtained in the same manner as for the LiF (Ti) crystal. The data were recorded in the same manner. After all the data were taken, the spacer was replaced with an organic crystal (NE109).

The organic scintillator (NE109) was used as the standard and the LiF (Ti) crystal was compared to it. The Hatch amplifier was adjusted to obtain an optimum signal of proper shape and amplitude from the NE109 crystal. The high voltage remained at 960 V. The differentiate and the integrate time constants each remained at 0.2 μ sec. The ND2200 ADC parameters were kept the same. The response spectrum for each source was recorded as had been done previously for the LiF (Ti) crystal.

The smaller diameter crystals (1 through 7) grown by the Bridgman-Stockbarger method were checked with the same procedures used to evaluate crystal 8. The responses of the individual crystals were not statistically greater than the response of the PM tube to the same radiation fields. Therefore, further consideration of the output of these small crystals will not be made in this paper.

(c) Determination of Crystal Efficiency—To determine the utility of the LiF (Ti) crystal in an instrument for measuring radiation dose rates, two parameters had to be compared to a known standard. In this experiment, the LiF (Ti) was compared to the organic crystal NE109 which has a known efficiency. Secondly, the response of the LiF (Ti) crystal should be similar to the response of tissue to the various energies of radiation discussed in Section III. In the procedure used to measure the response of LiF and NE109, different amplifier settings were required to obtain optimum signals for each crystal. Theoretically, if the high voltage is held constant, changing the amplifier settings will only shift the spectrum. However, this was not found to be true. Therefore, it was necessary to find a photon energy where

both voltage and amplifier settings could be the same for both crystals. This was necessary for the direct comparison of efficiencies of the two crystals. The only available source that met this requirement was cobalt-60, with an average energy of 1.25 MeV. For lower energy sources the LiF (Ti) (crystal 8) response was too low, and if higher voltages were used, the signal from the NE109 crystal was too large. The high-voltage setting for this phase of the experiment was 800 V. The amplifier pulse shape was set at 0.2 μ sec differentiation and 0.2 μ sec integration. The course gain was set at 1/16 and the fine gain at 0.25.

The source was covered with a 1.2-mm aluminum beta shield and placed in the holder below the shutter. Spectra for 1.25-MeV photons were obtained for the LiF crystal, the NE109 crystal, and the tube response. The data were recorded as previously discussed in Section II.B.4(b).

(d) Data Reduction—The data reduction of the spectra were done on a PDP 11/20 digital computer. The computer program provided for background subtraction, graphical presentation, and digital output of the total counts (see Appendix D for program). The data were fed into a PDP 11/20 off the Tally paper tape. The spectra were graphically printed out with a Calcomp plotter. The digital sum of the spectra were obtained from a high-speed Dec writer. The spectra are presented in Section III.A.

5. Optical Absorption (Crystal 8)

The optical absorption spectra of a cut and polished 0.5-cm-thick by 2.5-cm-diam LiF (Ti) crystal was measured on a Cary 14 recording

spectrophotometer by the Analytical Chemistry Group of the Lawrence Livermore Laboratory. The spectra were recorded on a Varian strip chart recorder. The crystal used for this analysis was cut from the same boule as the one used to determine the photon response. The results are plotted as a function of wavelength (nanometers) and percent absorption (see Section III.C for results).

6. Emission Spectrum (Crystal 8)

For the emission spectrum measurement, the crystal was excited with a 1000-W xenon arc lamp (Hanovia 976 C-1). The maximum wavelengths for the xenon excitation light peak were 240 nm and 315 nm. The measurements were made with a Baird Atomic, SF-1, fluorescent spectrophotometer with a double grating monochromator optical system. The slits were set at 122, 380, 232, and 450 nm, respectively, for each excitation peak. The detector for both excitation and emission was an Amprex 56TUVT, with an S-2C photocathode PM tube. The PM tube signal was amplified on a Log Keithly picoammeter and was recorded on a strip chart recorder. The PM tube high voltage was set at 2700 V. The results of the emission spectrum are presented in Section III.D. The excitation spectrum of the LiF (Ti) crystal was measured at the same time, and is also presented in Section III.D.

III. RESULTS

A. Response of LiF (Ti) to Six Discrete Photon Energies

The response of the LiF (Ti) crystal to the six discrete photon energies* after data reduction on the PDP 11/20, is graphically presented in Figs. 12 through 17. The graphical data are expressed as counts per channel as a function of energy. The counts are total counts per 100 or 1000 sec, minus a normalized background spectrum. The spectrum for each energy was totaled, and the results are given in Table 5. Figure 18 is a typical tube response spectrum and is the response of the PM tube to 662-MeV photons. The specific data for the nuclides used for the crystal response are given in Appendix E.

Table 5. Net response of the LiF crystal to various photon energies.

Source	E (keV)	Time (sec)	Counts (tube response)	Counts (LiF)
¹⁰⁹ Cd	22.5 + 88	1000	1.5×10^6	3.996×10^6
²⁴¹ Am	60 + 17	1000	1.15×10^6	5.05×10^5
²⁰³ Hg	279	1000	1.07×10^6	7.65×10^5
¹³⁷ Cs	662	1000	2.2×10^6	4.25×10^6
⁵⁴ Mn	835	1000	2.2×10^6	6.13×10^6
⁶⁰ Co	1250	1000	4.54×10^6	2.13×10^7

*Note: Due to the close proximity of the 1.17- and 1.33-MeV photon peaks of ⁶⁰Co, and since each peak has the same abundance as a single photon peak, a 1.25-MeV effective energy with a 200% abundance was assumed for all response calculations.

Fig. 12. Measured response of the LiF crystal to 22- and 88-keV photons of ^{109}Cd .

Fig. 13. Measured response of the LiF crystal to 17- and 60-keV photons of ^{241}Am .

Fig. 14. Measured response of the LiF crystal to 279-keV photons of ^{203}Hg .

Fig. 15. Measured response of the LiF crystal to 662-keV photons of ^{137}Cs .

Fig. 16. Measured response of the LiF crystal to 835-keV photons of ^{54}Mn .

Fig. 17. Measured response of the LiF crystal to 1117- and 1332-keV photons of ^{60}Co .

Fig. 18. Measured response of the PM tube to the 662-keV photons of ^{137}Cs .

An example of a raw PHA spectrum for a LiF (Ti) response to 22- and 88-keV photons of ^{109}Cd is presented in Fig. 19. Figure 20 is the spectrum response of the tube to 662-keV photons.

The total photon/cm²/sec flux of each nuclide was computed and normalized to the output of ^{60}Co (see Table 6). The response of the crystal in total counts per spectrum for each source was normalized to correspond to the flux of each source (see Table 6). Figure 21 is a graphical presentation of normalized counts as a function of the energy spectrum. Figure 22 is a graphical presentation of normalized counts divided by the energy.

Table 6. Theoretical normalized response of each nuclide and normalized response of the crystal in total counts.

Source	μCi	Photons/Ci	Photons/sec	Normalized ^{60}Co photons (counts/cm ² -sec)	Normalized response (counts)
^{60}Co	13.27	2.0	9.8×10^5	4×10^3	2.11×10^7
^{54}Mn	10.70	1.0	3.96×10^5	1.6×10^3	1.49×10^7
^{137}Cs	11.27	0.85	3.54×10^5	1.44×10^3	1.17×10^7
^{203}Hg	5.49	0.77	1.56×10^5	6.36×10^3	4.88×10^6
^{241}Am	11.30	0.72 ^a	3.02×10^5	1.22×10^3	6.46×10^6
^{109}Cd	93.80	0.96 ^b	3.33×10^6	1.36×10^4	1.18×10^6

^a $^{241}\text{Am} = 60 + 17\text{-keV photons.}$

^b $^{109}\text{Cd} = K_{\alpha} + K_{\beta} + 88\text{-keV photons.}$

A theoretical tissue dose was calculated for each of the radioactive nuclides. The parameters were established so that the dose

Fig. 19. Measured response of the LiF crystal to 22.5- and 88-keV photons (raw spectra).

Fig. 20. Measured PM tube response to 662-keV photons (raw spectra).

Fig. 21. Response of the LiF (Ti) crystal, normalized to ^{60}Co .

Fig. 22. Response of the LiF (Ti) crystal divided by the energy, normalized to ^{60}Co .

from each nuclide could be normalized as was the crystal response. The calculations for the theoretical tissue dose are given in Eqs. (3) through (7).

$$I_0(r, E) = \frac{S}{4\pi r^2} \quad (3)$$

$$S = 3.7 \times 10^{10} \text{ CE} \quad (4)$$

$$I_0 = 2.96 \times 10^9 \text{ CE (MeV/cm}^2\text{/sec)} \quad (5)$$

where

E = energy of photons in MeV,

r = the distance in cm,

C = the curies of the nuclide.

If the dose rate from a point source is defined as the energy absorbed per unit volume per unit time at the point of measurement, then the dose rate R at distance r is defined by

$$R = \mu_a I_0(r, E) = \frac{2.96 \times 10^9 \mu_a \text{ CE}}{r^2} \quad (6)$$

where

μ_a = the linear absorption coefficient,

R = MeV/cm³/sec.

If attenuation by the median is considered, the expression for R in Eq. (6) is multiplied by $e^{-\mu r}$ where μ = the linear attenuation coefficient.

The air attenuation over the energies considered is insignificant, and will not be considered for the theoretical dose. To obtain absorbed

dose rates in the more common units of rad/hr, Eq. (6) is multiplied by Q which is defined in Eq. (7) as

$$Q = \frac{1}{\rho} \frac{1.6 \times 10^{-6}}{1 \text{ MeV}} \text{ erg} \times \frac{1 \text{ rad}}{100 \text{ erg/g}} \times \frac{3.6 \times 10^3 \text{ sec}}{\text{hr}} . \quad (7)$$

Therefore,

$$R_d = QR,$$

$$R_d = 2.96 \times 10^9 \text{ CE} \times 5.76 \times 10^{-5} \times u_a/\rho \frac{\text{rad}}{\text{hr}} . \quad (8)$$

The theoretical dose to 1-cm-thick tissue and the crystal response at the photon energies used for this research are given in Table 7. The ratio of the theoretical to the crystal response is presented graphically in Fig. 23.

Table 7. Theoretical tissue dose for various energies.

E	Dose to tissue (rad/hr)	Crystal response
22.5 keV (eff)	2.032×10^{-3}	3,996,080
60 keV = 17 keV	1.12×10^{-4}	505,390
279 keV	2.485×10^{-4}	765,343
662 keV	1.399×10^{-3}	4,251,802
835 keV	1.925×10^{-3}	6,131,515
1250 keV (eff)	6.666×10^{-3}	21,264,674

The response of the LiF (Ti) crystal in terms of dose rate per counts per minute were calculated from the data in Table 7. The crystal response measured at 279 to 1250 keV was determined to be $5 \mu\text{rad/hr}$ per 1000 counts/min. This was based on a gross count of

Fig. 23. Relative response of LiF (crystal 8) to the theoretical tissue dose.

$25 \times 10^6/1000$ sec, and a tube response count of $4.5 \times 10^6/1000$ sec.

The mean signal response was 1.25×10^6 counts/min.

By the formula given by Prevo,⁶⁸ the minimum detectable count rate was determined from

$$\text{MDC} = \frac{1}{R} \left[3.29 \sqrt{\frac{B}{T}} + \frac{2.7}{T} \right] \quad (9)$$

where

R = the sensitivity (counts/min/ μ rad/hr),

B = background (counts/min),

T = counting time (min) [counting time = RC time constant of meter (0.2 min)].

The MDC is calculated at the 95% confidence level.

The minimum detectable dose rate is $\sim 14 \mu\text{rad/hr}$. This assumed that the tube response followed a normal Gaussian distribution. Because of possible errors due to unexplained response as a function of the time of day, this factor will be considered in both Section III.B and Section IV.

The efficiency of LiF (Ti) was determined by direct comparison to an organic scintillator NE109 of known efficiency. The efficiency was compared only at ⁶⁰Co energies. The fact that the voltage and amplifier settings were not optimum for the LiF (Ti) crystal was discussed in Chapter III. The mean total counts for LiF (Ti) was 2.87×10^5 counts/100 sec; the mean total counts for NE109 was 1,009 $\times 10^6$ counts/100 sec, and the tube response was 8.56×10^4 counts/100 sec. All counts were taken on consecutive days at the same time period to minimize error due to background (see Section III.B). The

net counts for the NE109 scintillator was 9.24×10^5 , and the net counts for the LiF (Ti) crystal was 2.01×10^5 . The efficiency of the LiF (Ti) compared to NE109 is 21.7% and 13.7% compared to anthracene at the voltage and amplifier settings given in Section II.

B. Error Analysis

The mean was determined for both the tube and LiF crystal response at each datum point. All data were calculated at the 95% confidence level, unless otherwise stated. The 2σ values in units of percent error for each data set and the results are given in Table 8.

Table 8. Experimental error analysis results.

Data set	Signal error (%)	Source error (%)	Tube response (%)	Total error (%)
^{60}Co	± 2	± 3.5	± 1.3	± 4.25
^{54}Mn	± 3	± 3.5	± 3.6	± 5.8
^{137}Cs	± 1	± 3.5	± 1	± 3.8
^{203}Hg	± 1	± 3.5	± 1.85	± 4.1
^{109}Cd	± 1	± 3.5	± 1.3	± 3.9
^{241}Am	± 1	± 3.5	± 1	± 3.8

The mean was calculated by

$$\bar{y} = \frac{1}{N} \sum_{i=1}^N y_i \quad (10)$$

The standard deviation was calculated by

$$\sigma \approx s = \left(\frac{1}{N-1} \right) \sum [(y - \bar{y})^2]^{1/2} \quad (11)$$

Except for statistical counting errors, other errors were not calculated since all are common to both tube and crystal response. It was noted that over a period of a day (0800 to 1700 hr) there was an approximately 40% significant difference in count rate.

The error in the difference between 1-cm air and 1-cm LiF for the tube response at the energies studied (279 and 1200 keV) was less than 1%, and therefore was neglected. It was also noted that the 88-keV energy photons from ^{109}Cd and the 17-keV x-ray component from ^{241}Am caused these data points to be questionable.

The error for the efficiency of the LiF crystal is given by

$$\frac{\bar{y}_c \pm \bar{y}_{ce} \text{ error}}{\bar{y}_o \pm \bar{y}_{oe} \text{ error}} = \frac{\bar{y}_c}{\bar{y}_o} \left\{ 1 \pm \left[\frac{(\bar{y}_{ce})^2}{(\bar{y}_c)^2} + \frac{(\bar{y}_{oe})^2}{(\bar{y}_o)^2} \right]^{1/2} \right\} \quad (12)$$

where

$\bar{y}_o$ = mean for response of organic scintillator,

$\bar{y}_c$ = mean for response of LiF crystal,

$\bar{y}_{oe} = 2\sigma$ and $\sigma = \sqrt{\bar{y}_o}$,

$\bar{y}_{ce} = 2\sigma$ and $\sigma = \sqrt{\bar{y}_c}$.

Therefore, the efficiency is equal to $21.7\% \pm 0.3\%$.

The determination of the minimum detectable dose rate at the 95% confidence level was given for a normal distribution, as stated in Section IV.A. The response of the tube and the crystal remained relatively constant over short periods of time, permitting use of Prevo's formula. However, if the statistical variances in the background counts were greater, the formula would require modification. No error analyses are presented for the absorption and emission spectra since they are qualitative.

C. Optical Absorption

Figure 24 shows the relative transmittance of the LiF (Ti) crystal. This figure is compared to Figs. 25 and 26. The earlier investigation by Ballard⁶⁹ shows optical absorption at 200 nm and a broadening at the base at approximately 290 nm, which is almost identical to Fig. 24. Zimmerman *et al.*⁷⁰ reported, as shown in Fig. 26, only a single absorption band for LiF (Ti) crystals. It is noted that the LiF (Ti) crystals reported by Jones were grown in dry argon and that the crystal prepared for this investigation was allowed to stand in air for several months.

D. Photoluminescence of LiF (Ti)

The photoluminescent spectrum (Fig. 27) of the crystal used in this research is comparable to that reported by Jones.⁷⁰ Although the excitation was at 253.7 nm for the work by Jones as compared to 240 and 315 nm for this research, the emission spectra for both are centered at approximately 400 nm. The emission spectrum for the LiF (Ti) crystal was measured at room temperature, and is comparable with the 300°K spectrum of Jones. No other emission peaks were noted for this crystal. Based on early work⁷⁰ and later private communications with Jones, the 400-nm emission peak is hypothesized to be the result of (Ti) color centers. The emission spectrum of crystal (8) therefore is commensurate with the Ti, as determined in crystal (8) by emission spectrographic methods previously discussed in Chapter II.

Fig. 24. Ultraviolet absorption spectra of LiF crystal ($\sim 1/2$ -in. thick).

Fig. 2.. Ultraviolet absorption spectra reported by Ballard.⁶⁹

Fig. 26. Ultraviolet absorption spectrum reported by Jones et al.⁷⁰

Fig. 27. Emission and excitation spectra for crystal (8).

IV. DISCUSSION AND CONCLUSION

A. Discussion

1. Optical Absorption and Emission Spectra

The absorption band associated with the Ti^{+2} ion in the LiF lattice centered at 200 nm^{71} was observed in crystal(8). This crystal section, taken from the center of the boule, has a visible darkening that indicated the presence of Ti ions. The broadening of the base of the absorption band was caused by production in air or prolonged exposure of the crystal to the atmosphere. This is corroborated by Toy⁷¹ who reported an absorption band at 250 nm due to O_2 . Consequently, there should be little or no effect on optical transmission since the emission band is at a higher wavelength (400 nm).

The emission spectra based on the work by Jones and others⁷⁰ indicate that the ion responsible for the 400-nm peak is Ti. Therefore, an increase in Ti ion concentration should result in an increase in photon output as a result of the increase in density of unoccupied activator sites (N_a). The efficiency of the phosphor $dL/dE \approx 1/\epsilon(n_o/n_e)SP_L P_e$ is directly proportional to N_a and therefore proportional to the Ti concentration present in the LiF host.

2. The Scintillation Response of LiF (Ti)

One of the major difficulties in obtaining higher count rates was the low concentration of Ti ions and the apparent consistency of the Ti ion concentration through the LiF crystal, as evidenced in the spectrochemical analysis of the crystal (see Appendix C). A higher count rate would permit use of more sophisticated electronic pulse shaping and pulse discrimination than now employed. A more serious problem that is directly related to the color center was the apparent

magnitude of the light pulse or the energy conversion process of the color center. There may have been sufficient pulses, but a great many were of such low intensity that they were electronically rejected by the PHA ADC. The problem may preclude use of Ti as an activator in LiF crystals. However, one question of major importance needs to be answered before Ti as an activator is totally rejected; namely, the electronic state of Ti (d^0 , d^1 or d^2) must be determined. The light intensity, a function of the conversion process that is a result of energy level transitions, may be radically changed for different atomic states of Ti. It may also result in higher or lower concentrations of Ti ions in the crystal.

The signal-to-tube response was an extremely critical parameter of the crystal research. The largest portion of total counts occurred in the first few channels, which may be a direct result of the energy conversion previously discussed. It was also noted that the true signal had a risetime comparable to that of the tube response and thermionic noise of the PM tube. The practical result was that no pulse shape discrimination or energy pulse discrimination could be employed.

A solution to this problem would be coincidence counting. A method could be used by which tube response could be essentially cancelled with only the true signal being sent to the PHA. This would also allow for a wider range of voltage selections and provide better response spectra.

The problem of crystal signal and tube response variance over a period of time cannot be readily accounted for. It was noted that background and the tube response also varied proportionally over

a 12-hr period with a peak between 9 a. m. and 10 a. m. This response variance does not appear to be a direct function of room temperature. Signal and tube response and background taken at the same time period showed only minor variance. However, the errors would be comparatively smaller without this large variance.

The energy response of LiF relative to tissue has been shown to be excellent above 279 keV. However, at the two data points, ^{109}Cd 22.5 keV and 88 keV and ^{241}Am 60 keV and 17 keV, the crystal response does not agree with the tissue response. The deviation of the LiF crystal response from the theoretical at low energies may have resulted from attenuation in the crystal, the energy transport of excitons, subsequent conversion to light, and other factors that may not have been considered. It will be necessary to verify the low-energy response, which can be accomplished using fluorescent x-ray techniques.

The response of LiF apparently is consistent with the model of Murray and Meyer³⁶ shown in Eq. (13) and with Eq. (2) by Ramm⁵¹ for phosphor response.

$$S_y = \frac{E_{PY}}{E_{WX}} \left(\frac{n_o}{n_e} \right) (f_{xy}) (q_{oy}) \quad (13)$$

(see Appendix F, Eq. (F-24) for details).

An attempt to verify the model will require measurement of the response of crystals of varying concentrations of Ti. It would also be desirable to try other activator ions, including Tl.

B. Conclusions

1. It is difficult to grow LiF crystals doped with activator sites.
2. LiF (Ti) does scintillate, but only at 17% compared to anthracene.
3. The energy response is equivalent to the response of tissue to photons over the measured range of 279 to 1250 keV. There are apparent anomalies and/or experimental error at the 60-keV and 22.5-keV data point examined.
4. Because the concentration gradient of (Ti) in the host crystal varied between 1 and 60 ppm, it will be necessary to grow crystals of more uniform concentration in the range of 40 to 100 ppm. Since the evidence suggests Ti is the color center, the higher concentration should yield a more efficient system.
5. The tube response cannot be discriminated against in the experimental conditions investigated. It is apparent that coincidence counting may be the most effective way to solve this problem, and it should be investigated.

APPENDIX A
 FORTRAN COMPUTER PROGRAM FOR CALCULATING
 THE RESPONSE OF LiF RELATIVE
 TO SOME STANDARD MATERIAL

```

PROGRAM RK(IN,TAPE2=IN,12,TAPE3=OP)
C THIS CODE CALCULATES THE RESPONSE OF LITHIUM FLUORIDE RELATIVE
C TO SOME STANDARD MATERIAL FOR A SPECIFIED THICKNESS (X)
C THE CROSS SECTIONS ARE READ FROM A FILE (IN). THE STANDARD
C MATERIAL CROSS SECTIONS ARE IN CM2/GM.
CALL CHANGE(3H+RK)
CALL DEVICE(6HCREATE,2HDP,10000)
DIMENSION E(20),PEL(20),COMPL(20),PPL(20)
DIMENSION PELFX(20),COMPLX(20),PPFX(20),PELXT(20)
DIMENSION COMPLFX(20),PELFX(20),XFCOMP(20),ATEN(20)
DIMENSION ATTFACT(20),RESPD(20),ABSFAC(20)
DIMENSION XCOMPL(20),XPEL(20),XPPL(20)
DIMENSION XCOMPLFX(20),XPELFX(20),XPPLFX(20)
DIMENSION RESPON(20),ATENSTD(20),ATFSTD(20)
DIMENSION ABSSTD(20),RESPATT(20)
C READ IN THE CROSSSECTIONS
READ(2,10)(L(I),COMPL(I),PEL(I),PPL(I),I=1,18)
READ(2,10)(L(I),COMPLFX(I),PELFX(I),PPFX(I),I=1,18)
10 FORMAT(F5,3,3X,E11.4,3X,E11.4,3X,E11.4)
DO 30 I=1,18
  READ(2,11) XFCOMP(I)
30 CONTINUE
11 FORMAT(F7,4)
DO 33 I=1,18
  READ(2,32) ATENSTD(I)
33 CONTINUE
C READ IN THE ENERGY TRANSFER CROSS SECTIONS FOR THE STANDARD
C
DO 34 I=1,18
  READ (2,32) ABSSTD(I)
34 CONTINUE
32 FORMAT(F7,4)
RHO=3.601
RHOSTD=.0012
X=1.
Z=.602/(6.94+19.0)
DO 100 I=1,18

```

C THE CROSS SECTIONS FROM MCMASTER CARDS ARE IN HARNS/ATOM
C

```

PELX(I)=C*(PEL(I)+PEFX(I))
COMPLX(I)=C*(COMPL(I)+COMPFX(I))
PPLX(I)=C*(PPL(I)+PPFX(I))
PP=1.,511/E(I)
ATEN(I)=PELX(I)+COMPLX(I)+PPLX(I)
ATTFACT(I)=(1.-EXP(-ATEN(I)*RHO*X))/(ATEN(I)*RHO*X)
ABSFAC(I)=(ELFX(I)+XCOMPI(I)+COMPIFX(I)+PPP*PPLX(I)
ATFSTD(I)=(1.-EXP(-ATENST(I)*RHUSTD*X))/(ATENST(I)*RHUSTD*X)
RESP(I)=ATTFACT(I)*ABSFAC(I)/ATFSTD(I)/ABSTSD(I)
100 CONTINUE
DO 102 I=1,18
102 RESP(I)=RESP(I)/RESP(18)
A=.602/6.94
B=.602/19.0
DO 101 I=1,18
XCOMPL(I)=A*COMPL(I)
XPEL(I)=A*PEL(I)
XPPL(I)=A*PPL(I)
XCOMPFX(I)=B*COMPFX(I)
XPEFX(I)=B*PEFX(I)
101 XPPFX(I)=B*PPFX(I)
WRITE(3,12)
12 FORMAT(//,3X,*CROSS SECTIONS FOR LITHIUM - CM2/GM*//)
WRITE(3,13)
13 FORMAT(5X,*ENERGY*,6X,*PHOTO*,6X,*COMPTON*,6X,*PAIR PROD*,//)
WRITE(3,24)(E(I),XCOMPL(I),XPEL(I),XPPL(I),I=1,18)
WRITE(3,14)
14 FORMAT(//,3X,*CROSS SECTIONS FOR FLUORINE - CM2/GM*//)
WRITE(3,13)
WRITE(3,24)(E(I),XCOMPFX(I),XPEFX(I),XPPFX(I),I=1,18)
24 FORMAT(2X,F5.3,3X,E11.4,3X,E11.4,3X,E11.4)
WRITE(3,15)
15 FORMAT(//,3X,*ATTENUATION AND ABSORPTION FACTORS FOR*
1 * LF AND STANDARD*//)
WRITE(3,16)
16 FORMAT(5X,*ATTFACT*,10X,*ABSFAC*,10X,*ATFSTD*,12X,*ABSTSD*//)
DO 17 I=1,18
WRITE(3,18)(ATTFACT(I),ABSFAC(I),ATFSTD(I),ABSTSD(I))
18 FORMAT(3X,E11.4,6X,E11.4,6X,E11.4,7X,E11.4)
17 CONTINUE
WRITE(3,25)
25 FORMAT(//,*THE RESPONSE OF LITHIUM FLUORIDE RELATIVE*,
* * TO STD NORMALIZED TO 1 AT 1 MEV*//)
WRITE(3,19)(E(I),RESP(I),I=1,18)
19 FORMAT(3X,F5.3,5X,F11.4)
20 CONTINUE
CALL EXIT
END

```

APPENDIX B

CROSS SECTION DATA

CROSS SECTIONS FOR LiF, TISSUE AND AIR.

ATTENUATION FACTORS AND ABSORPTION FACTORS FOR LiF,
TISSUE AND AIR.

RESPONSE OF LiF RELATIVE TO TISSUE AND AIR FOR VARIOUS
THICKNESSES OF MATERIAL .

~~CROSS SECTIONS FOR LITHIUM - 5MP/AM~~ Tissue - 0.5 cm-

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.4425E-01	2.8844E-02	.0E+00
.020	1.4877E-01	1.0089E-02	.0E+00
.030	1.4955E-01	2.3837E-03	.0E+00
.040	1.4712E-01	8.6050E-04	.0E+00
.050	1.4382E-01	3.9251E-04	.0E+00
.060	1.4035E-01	2.0765E-04	.0E+00
.080	1.3367E-01	7.6941E-05	.0E+00
.100	1.2760E-01	3.6033E-05	.0E+00
.150	1.1520E-01	9.3770E-06	.0E+00
.200	1.0565E-01	3.7152E-06	.0E+00
.300	9.1948E-02	1.0600E-06	.0E+00
.400	8.2363E-02	4.5359E-07	.0E+00
.500	7.5224E-02	2.4089E-07	.0E+00
.600	6.9586E-02	1.4634E-07	.0E+00
.800	6.1126E-02	6.9005E-08	.0E+00
1.000	5.4952E-02	3.9841E-08	.0E+00
1.500	4.4643E-02	1.9590E-08	3.4023E-05
2.000	3.8082E-02	1.1839E-08	1.3974E-04

CROSS SECTIONS FOR FLUORINE - CM2/GM

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.3402E-01	2.1124E+00	.0E+00
.020	1.4309E-01	8.3234E-01	.0E+00
.030	1.5063E-01	2.2131E-01	.0E+00
.040	1.5221E-01	8.6244E-02	.0E+00
.050	1.4961E-01	4.1570E-02	.0E+00
.060	1.4904E-01	2.2927E-02	.0E+00
.080	1.4358E-01	9.0110E-03	.0E+00
.100	1.3786E-01	4.3945E-03	.0E+00
.150	1.2525E-01	1.2141E-03	.0E+00
.200	1.1520E-01	4.9649E-04	.0E+00
.300	1.0047E-01	1.4542E-04	.0E+00
.400	9.0110E-02	6.2608E-05	.0E+00
.500	8.2347E-02	3.3142E-05	.0E+00
.600	7.6201E-02	1.9974E-05	.0E+00
.800	6.6949E-02	9.2105E-06	.0E+00
1.000	6.0200E-02	5.1709E-06	.0E+00
1.500	4.8914E-02	2.5305E-06	1.1303E-04
2.000	4.1728E-02	1.5324E-06	4.6159E-04

ATTENUATION AND ABSORPTION FACTORS FOR LF AND STANDARD

ATTFACT	ABSFAC	ATFSTD	ABSSTU
3,1273E-01	1,5585E+00	7,0660E-01	1,3600E+00
5,4595E-01	1,1758E-01	8,4197E-01	5,4400E-01
7,5442E-01	1,7056E-01	9,2007E-01	1,5400E-01
8,2971E-01	7,3462E-02	9,4049E-01	6,7780E-02
8,5514E-01	4,2502E-02	9,4836E-01	4,0640E-02
8,5620E-01	3,0611E-02	9,5233E-01	3,1280E-02
8,7920E-01	2,3122E-02	9,5656E-01	2,5580E-02
8,8514E-01	2,1874E-02	9,5915E-01	2,5200E-02
8,9666E-01	2,3136E-02	9,6366E-01	2,7600E-02
9,0482E-01	2,4719E-02	9,6676E-01	2,9700E-02
9,1657E-01	2,6579E-02	9,7107E-01	3,1740E-02
9,2473E-01	2,7320E-02	9,7390E-01	3,2500E-02
9,3094E-01	2,7568E-02	9,7621E-01	3,2700E-02
9,3588E-01	2,7368E-02	9,7796E-01	3,2600E-02
9,4337E-01	2,6745E-02	9,8060E-01	3,1800E-02
9,4889E-01	2,5868E-02	9,8253E-01	3,0800E-02
9,5812E-01	2,3700E-02	9,8576E-01	2,8100E-02
9,5387E-01	2,1908E-02	9,8775E-01	2,5700E-02

THE
RESPONSE OF LITHIUM FLUORIDE RELATIVE TO STD NORMALIZED TO 1 AT

1 MEV

.015	6,2530E-01
.020	9,0798E-01
.030	1,1344E+00
.040	1,1802E+00
.050	1,1552E+00
.050	1,1002E+00
.090	1,0263E+00
.100	9,8763E-01
.150	9,6162E-01
.200	9,6038E-01
.300	9,7562E-01
.400	9,8399E-01
.500	9,9116E-01
.600	9,9047E-01
.800	9,9753E-01
1,000	1,0000E+00
1,500	1,0307E+00
2,000	1,0256E+00

~~CROSS SECTIONS FOR LITHIUM~~ • CM²/GM Tissue 1 cm -

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.4425E-01	2.8044E-02	.0E+00
.020	1.4877E-01	1.0088E-02	.0E+00
.030	1.4955E-01	2.3837E-03	.0E+00
.040	1.4712E-01	8.6050E-04	.0E+00
.050	1.4382E-01	3.9251E-04	.0E+00
.060	1.4035E-01	2.0705E-04	.0E+00
.080	1.3367E-01	7.6941E-05	.0E+00
.100	1.2760E-01	3.6033E-05	.0E+00
.150	1.1520E-01	9.3779E-06	.0E+00
.200	1.0565E-01	3.7152E-06	.0E+00
.300	9.1948E-02	1.0600E-06	.0E+00
.400	8.2363E-02	4.5350E-07	.0E+00
.500	7.5224E-02	2.4082E-07	.0E+00
.600	6.9586E-02	1.4634E-07	.0E+00
.800	6.1128E-02	6.9065E-08	.0E+00
1.000	5.4952E-02	3.9841E-08	.0E+00
1.500	4.4643E-02	1.9590E-08	3.4023E-05
2.000	3.8082E-02	1.1839E-08	1.3974E-04

CROSS SECTIONS FOR FLUORINE • CM²/GM

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.3402E-01	2.1124E+00	.0E+00
.020	1.4309E-01	8.3234E-01	.0E+00
.030	1.5063E-01	2.2131E-01	.0E+00
.040	1.5221E-01	8.6244E-02	.0E+00
.050	1.4964E-01	4.1570E-02	.0E+00
.060	1.4904E-01	2.2927E-02	.0E+00
.080	1.4356E-01	9.0110E-03	.0E+00
.100	1.3786E-01	4.3945E-03	.0E+00
.150	1.2525E-01	1.2141E-03	.0E+00
.200	1.1520E-01	4.9642E-04	.0E+00
.300	1.0047E-01	1.4542E-04	.0E+00
.400	9.0110E-02	6.2608E-05	.0E+00
.500	8.2347E-02	3.3142E-05	.0E+00
.600	7.6201E-02	1.9074E-05	.0E+00
.800	6.6949E-02	9.2106E-06	.0E+00
1.000	6.0200E-02	5.1707E-06	.0E+00
1.500	4.8914E-02	2.5365E-06	1.1303E-04
2.000	4.1728E-02	1.5324E-06	4.6158E-04

ATTENUATION AND ABSORPTION FACTORS FOR LF AND STANDARD

ATTFACT	ABSFAC	ATFSTN	ABSSTD
1.6380E-11	1.5585E+00	5.2187E+01	1.3680E+00
3.4284E-01	1.1758E-01	7.1568E+01	3.4400E+01
5.9972E-01	1.7056E-01	8.4853E+01	1.5480E+01
6.9693E-01	7.3462E-02	8.8565E+01	6.7700E+02
7.3795E-01	4.2502E-02	9.0024E+01	4.0988E+02
7.5572E-01	3.0611E-02	9.0766E+01	3.1200E+02
7.7576E-01	2.3122E-02	9.1561E+01	2.5500E+02
7.9780E-01	2.1874E-02	9.2051E+01	2.5200E+02
8.0781E-01	2.3136E-02	9.2907E+01	2.7600E+02
8.2183E-01	2.4719E-02	9.3498E+01	2.9700E+02
8.4217E-01	2.6579E-02	9.4325E+01	3.1700E+02
8.5692E-01	2.7320E-02	9.4882E+01	3.2500E+02
8.5816E-01	2.7568E-02	9.5317E+01	3.2700E+02
8.7718E-01	2.7368E-02	9.5656E+01	3.2600E+02
8.9097E-01	2.6745E-02	9.6171E+01	3.1800E+02
9.0182E-01	2.5868E-02	9.6547E+01	3.0800E+02
9.1856E-01	2.3700E-02	9.7179E+01	2.8100E+02
9.2947E-01	2.1908E-02	9.7570E+01	2.5700E+02

THE
RESPONSE OF LITHIUM FLUORIDE RELATIVE TO STD NORMALIZED TO 1 AT
1 MEV

.015	4.5880E-01
.020	6.9367E-01
.030	9.9845E-01
.040	1.0892E+00
.050	1.0859E+00
.060	1.0419E+00
.080	9.7993E-01
.100	9.4732E-01
.150	9.2911E-01
.200	9.3280E-01
.300	9.5487E-01
.400	9.6638E-01
.500	9.7942E-01
.600	9.8196E-01
.800	9.9388E-01
1.000	1.0000E+00
1.500	1.0169E+00
2.000	1.0358E+00

~~CROSS SECTIONS FOR LITHIUM - CM²/GM~~ Tissue = 1.27 cm

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.4425E-01	2.8044E-02	.0E+00
.020	1.4677E-01	1.0088E-02	.0E+00
.030	1.4955E-01	2.3837E-03	.0E+00
.040	1.4712E-01	8.6050E-04	.0E+00
.050	1.4382E-01	3.9251E-04	.0E+00
.060	1.4035E-01	2.0766E-04	.0E+00
.080	1.3367E-01	7.6941E-05	.0E+00
.100	1.2760E-01	3.6033E-05	.0E+00
.150	1.1920E-01	9.3770E-06	.0E+00
.200	1.0565E-01	3.7152E-06	.0E+00
.300	9.1948E-02	1.0600E-06	.0E+00
.400	8.2363E-02	4.5350E-07	.0E+00
.500	7.5224E-02	2.4089E-07	.0E+00
.600	6.9986E-02	1.4634E-07	.0E+00
.800	6.1128E-02	6.9065E-08	.0E+00
1.000	5.4952E-02	3.9841E-08	.0E+00
1.500	4.4643E-02	1.9590E-08	3.4023E-05
2.000	3.8082E-02	1.1839E-08	1.3974E-04

CROSS SECTIONS FOR FLUORINE - CM²/GM

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.3402E-01	2.1124E-02	.0E+00
.020	1.4309E-01	8.3234E-03	.0E+00
.030	1.5063E-01	2.2131E-03	.0E+00
.040	1.5221E-01	8.6244E-04	.0E+00
.050	1.4961E-01	4.1570E-04	.0E+00
.060	1.4904E-01	2.2927E-04	.0E+00
.080	1.4356E-01	9.0110E-05	.0E+00
.100	1.3786E-01	4.3946E-05	.0E+00
.150	1.2525E-01	1.2141E-05	.0E+00
.200	1.1920E-01	4.9449E-06	.0E+00
.300	1.0047E-01	1.4542E-06	.0E+00
.400	9.0110E-02	6.2608E-07	.0E+00
.500	8.2347E-02	3.3142E-07	.0E+00
.600	7.6201E-02	1.9974E-07	.0E+00
.800	6.6949E-02	9.2106E-08	.0E+00
1.000	6.0200E-02	5.1709E-08	.0E+00
1.500	4.8914E-02	2.5385E-08	1.1303E-04
2.000	4.1728E-02	1.5324E-08	4.6158E-04

ATTENUATION AND ABSORPTION FACTORS FOR LF AND STANDARD

ATTFACT	ABSFAC	ATFSTD	ABSTD
1,2981E-01	1,5585E+00	4,5081E-01	1,3680E+00
2,7980E-01	1,1758E-01	6,5833E-01	5,4400E-01
5,3188E-01	1,7056E-01	8,1305E-01	1,5400E-01
6,3749E-01	7,3462E-02	8,5783E-01	6,7700E-02
6,5333E-01	4,2502E-02	8,7563E-01	4,0980E-02
7,0412E-01	3,0611E-02	8,8472E-01	3,1200E-02
7,2727E-01	2,3122E-02	8,9448E-01	2,5500E-02
7,4193E-01	2,1674E-02	9,0032E-01	2,5200E-02
7,6411E-01	2,3136E-02	9,1108E-01	2,7600E-02
7,8089E-01	2,4719E-02	9,1840E-01	2,9700E-02
8,0544E-01	2,6579E-02	9,2868E-01	3,1780E-02
8,2311E-01	2,7320E-02	9,3561E-01	3,2500E-02
8,3644E-01	2,7568E-02	9,4103E-01	3,2700E-02
8,4795E-01	2,7368E-02	9,4526E-01	3,2600E-02
8,6432E-01	2,6745E-02	9,5171E-01	3,1800E-02
8,7643E-01	2,5868E-02	9,5642E-01	3,0800E-02
8,9812E-01	2,3708E-02	9,6436E-01	2,8180E-02
9,1198E-01	2,1908E-02	9,6928E-01	2,5700E-02

THE

RESPONSE OF LITHIUM FLUORIDE RELATIVE TO STD NORMALIZED TO 1 AT

1 MEV

.015	4,2659E-01
.020	6,2645E-01
.030	9,4043E-01
.040	1,0473E+00
.050	1,0532E+00
.060	1,0141E+00
.080	9,5747E-01
.100	9,2767E-01
.150	9,1306E-01
.200	9,1909E-01
.300	9,4443E-01
.400	9,6046E-01
.500	9,7342E-01
.600	9,7759E-01
.800	9,9199E-01
1,000	1,0000E+00
1,500	1,0201E+00
2,000	1,0412E+00

~~CROSS SECTIONS FOR LITHIUM - CM²/GM~~ Air-0.5 cm

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.4425E-01	2.8044E-02	.0E+00
.020	1.4877E-01	1.0088E-02	.0E+00
.030	1.4955E-01	2.3837E-03	.0E+00
.040	1.4712E-01	8.6050E-04	.0E+00
.050	1.4382E-01	3.9251E-04	.0E+00
.060	1.4035E-01	2.0766E-04	.0E+00
.080	1.3367E-01	7.6941E-05	.0E+00
.100	1.2760E-01	3.6033E-05	.0E+00
.150	1.1520E-01	9.3770E-06	.0E+00
.200	1.0565E-01	3.7152E-06	.0E+00
.300	9.1949E-02	1.0600E-06	.0E+00
.400	8.2363E-02	4.5350E-07	.0E+00
.500	7.5224E-02	2.4002E-07	.0E+00
.600	6.9586E-02	1.4634E-07	.0E+00
.800	6.1128E-02	6.9065E-08	.0E+00
1.000	5.4952E-02	3.9801E-08	.0E+00
1.500	4.4643E-02	1.9590E-08	3.4023E-05
2.000	3.8082E-02	1.1639E-08	1.3974E-04

CROSS SECTIONS FOR FLUORINE - CM²/GM

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.3402E-01	2.1124E+00	.0E+00
.020	1.4309E-01	8.3234E-01	.0E+00
.030	1.5063E-01	2.2131E-01	.0E+00
.040	1.5221E-01	8.6244E-02	.0E+00
.050	1.4961E-01	4.1673E-02	.0E+00
.060	1.4904E-01	2.2927E-02	.0E+00
.080	1.4356E-01	9.0117E-03	.0E+00
.100	1.3786E-01	4.3945E-03	.0E+00
.150	1.2525E-01	1.2141E-03	.0E+00
.200	1.1520E-01	4.9649E-04	.0E+00
.300	1.0047E-01	1.4542E-04	.0E+00
.400	9.0110E-02	6.2609E-05	.0E+00
.500	8.2347E-02	3.3142E-05	.0E+00
.600	7.6201E-02	1.9974E-05	.0E+00
.800	6.6949E-02	9.2105E-06	.0E+00
1.000	6.0200E-02	5.1709E-06	.0E+00
1.500	4.8924E-02	2.5385E-06	1.1303E-04
2.000	4.1720E-02	1.5324E-06	4.6158E-04

ATTENUATION AND ABSORPTION FACTORS FOR LF AND STANDARD

ATTFACT	ABSFAC	ATFSTD	ABSTSD
3.1273E-11	1.5585E+00	9.9957E-01	1.2500E+00
5.4595E-01	.1750E-01	9.9979E-01	5.0200E-01
7.5442E-01	1.7056E-01	9.9990E-01	1.4500E-01
8.2971E-01	7.3462E-02	9.9993E-01	6.2200E-02
8.5514E-01	4.2502E-02	9.9994E-01	3.7600E-02
8.5620E-01	3.0611E-02	9.9995E-01	2.8700E-02
8.7820E-01	2.3122E-02	9.9995E-01	2.3400E-02
8.8519E-01	2.1874E-02	9.9995E-01	2.3100E-02
8.9666E-01	2.3136E-02	9.9996E-01	2.4900E-02
9.0482E-01	2.4719E-02	9.9996E-01	2.6600E-02
9.1631E-01	2.6579E-02	9.9997E-01	2.8700E-02
9.2473E-01	2.7320E-02	9.9997E-01	2.9500E-02
9.3094E-01	2.7566E-02	9.9997E-01	2.9900E-02
9.3588E-01	2.7368E-02	9.9998E-01	2.9600E-02
9.4337E-01	2.6745E-02	9.9999E-01	2.8800E-02
9.4839E-01	2.5868E-02	9.9998E-01	2.7900E-02
9.5812E-01	2.3700E-02	9.9998E-01	2.5500E-02
9.6387E-01	2.1900E-02	9.9999E-01	2.3400E-02

THE
RESPONSE OF LITHIUM FLUORIDE RELATIVE TO STD NORMALIZED TO 1 AT

1 MEV

.015	4.4338E-01
.020	7.6357E-01
.030	1.0221E+00
.040	1.1139E+00
.050	1.0987E+00
.060	1.0581E+00
.090	9.6337E-01
.100	9.5278E-01
.150	9.4701E-01
.200	9.5577E-01
.300	9.6477E-01
.400	9.7343E-01
.500	9.7561E-01
.600	9.8355E-01
.800	9.9597E-01
1.000	1.0000E+00
1.500	1.0122E+00
2.000	1.0257E+00

~~CROSS SECTIONS FOR LITHIUM - CM²/GM~~ Air 1 cm

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.4425E-01	2.8844E-02	.0E+00
.020	1.4877E-01	1.0088E-02	.0E+00
.030	1.4955E-01	2.3837E-03	.0E+00
.040	1.4712E-01	8.6050E-04	.0E+00
.050	1.4382E-01	3.9251E-04	.0E+00
.060	1.4035E-01	2.0765E-04	.0E+00
.080	1.3367E-01	7.6941E-05	.0E+00
.100	1.2760E-01	3.6033E-05	.0E+00
.150	1.1520E-01	9.3770E-06	.0E+00
.200	1.0565E-01	3.7152E-06	.0E+00
.300	9.1948E-02	1.0600E-06	.0E+00
.400	8.2363E-02	4.5350E-07	.0E+00
.500	7.5224E-02	2.4842E-07	.0E+00
.600	6.9586E-02	1.4634E-07	.0E+00
.800	6.1128E-02	6.9065E-08	.0E+00
1.000	5.4952E-02	3.9841E-08	.0E+00
1.500	4.4643E-02	1.2590E-08	3.4023E-05
2.000	3.8082E-02	1.1839E-08	1.3974E-04

CROSS SECTIONS FOR FLUORINE - CM²/GM

ENERGY	PHOTO	COMPTON	PAIR PROD
.015	1.3402E-01	2.1124E+00	.0E+00
.020	1.4309E-01	8.3234E-01	.0E+00
.030	1.5063E-01	2.2131E-01	.0E+00
.040	1.5221E-01	8.6244E-02	.0E+00
.050	1.4961E-01	4.1570E-02	.0E+00
.060	1.4904E-01	2.2927E-02	.0E+00
.080	1.4356E-01	9.0110E-03	.0E+00
.100	1.3786E-01	4.3945E-03	.0E+00
.150	1.2525E-01	1.2141E-03	.0E+00
.200	1.1520E-01	4.9649E-04	.0E+00
.300	1.0047E-01	1.4542E-04	.0E+00
.400	9.0110E-02	6.2608E-05	.0E+00
.500	8.2347E-02	3.3142E-05	.0E+00
.600	7.6201E-02	1.9974E-05	.0E+00
.800	6.6949E-02	9.2105E-06	.0E+00
1.000	6.0200E-02	5.1709E-06	.0E+00
1.500	4.8914E-02	2.5305E-06	1.4303E-04
2.000	4.1728E-02	1.5324E-06	4.6158E-04

ATTENUATION AND ABSORPTION FACTORS FOR LF AND STANDARD

ATTFACT	ABSFACT	ATFSTD	ABSSTD
1.5380E-01	1.5585E+00	9.9913E-01	1.2500E+00
3.4284E-01	.1758E-01	9.9958E-01	5.0200E-01
5.9972E-01	1.7056E-01	9.9981E-01	1.4500E-01
6.9693E-01	7.3462E-02	9.9986E-01	6.2200E-02
7.3755E-01	4.2502E-02	9.9988E-01	3.7600E-02
7.5572E-01	3.0611E-02	9.9989E-01	2.8700E-02
7.7576E-01	2.3122E-02	9.9990E-01	2.3400E-02
7.9760E-01	2.1874E-02	9.9991E-01	2.3100E-02
8.3731E-01	2.3136E-02	9.9992E-01	2.4900E-02
8.2153E-01	2.4719E-02	9.9993E-01	2.6600E-02
8.4217E-01	2.6579E-02	9.9994E-01	2.8700E-02
8.3692E-01	2.7320E-02	9.9994E-01	2.9500E-02
8.5816E-01	2.7568E-02	9.9995E-01	2.9900E-02
8.7718E-01	2.7368E-02	9.9995E-01	2.9600E-02
8.9097E-01	2.6745E-02	9.9998E-01	2.8800E-02
9.3122E-01	2.5868E-02	9.9996E-01	2.7900E-02
9.1856E-01	2.3700E-02	9.9997E-01	2.5500E-02
9.2947E-01	2.1908E-02	9.9997E-01	2.3400E-02

THE

RESPONSE OF LITHIUM FLUORIDE RELATIVE TO STD NORMALIZED TO 1 AT

1 MEV

.015	2.4462E-01
.020	5.0494E-01
.030	8.4436E-01
.040	9.8517E-01
.050	9.9782E-01
.060	9.6468E-01
.080	9.1743E-01
.100	8.9259E-01
.150	8.9775E-01
.200	9.1369E-01
.300	9.3342E-01
.400	9.4976E-01
.500	9.5794E-01
.600	9.7062E-01
.800	9.9059E-01
1.000	1.0000E+00
1.500	1.0217E+00
2.000	1.0414E+00

APPENDIX C — SPECTROCHEMICAL ANALYSIS REPORTS

Table C-1. Analysis of LiF crystals 1-8.

SPECTROCHEMICAL ANALYSIS REPORT
 LRL - LIVERMORE -- ANALYTICAL LABORATORY

SPECTROCHEMICAL ANALYSIS REPORT		Plate No.: 3054, 3047
LRL - LIVERMORE -- ANALYTICAL LABORATORY		Sample No.:
		SS-0116
		Submitted By:
		R. Kloepping
Sample Description:		Date Received:
Lithium Fluoride		Date Reported:
Samples 1 through 8		1-30-73
		2-7-73
		Analyst:
		E. Peck

Key: Numbers - ppm by weight in LiF
 N. d. - not detected

Analysis:	1	2	3	4	5	6	7	8
Ag	1	1	0.5	<0.5	<0.5	<0.5	0.5	1
Tl	n. d. <3	n. d. <3	n. d. <3	n. d. <3	n. d. <3	n. d. <3	n. d. <3	n. d. <3
Al	3	<3	<3	<3	<3	<3	<3	<3
Ca	<1	10	<1	<1	5	<1	<1	<1
Cr	3	<1	<1	<1	<1	<1	<1	<1
Cu	3	<3	<3	<3	<3	<3	<3	<3
Fe	<3	<3	<3	<3	100	<3	<3	<3 n. d.
Mg	15	3	3	6	3	3	1	<0.3 n. d.
Mn	5	1	10	1	2	5	1	<1 n. d.
Mo	1	1	1	1	<1	1	<1	<1 n. d.
Ni	5	300	<1	300	1000	20	1000	<1
Si	20	30	10	15	30	25	15	10
Sr	n. d. <0.1	n. d. <0.1	n. d. <0.1	n. d. <0.1	n. d. <0.1	0.5	n. d. <0.1	0.5 n. d.
Ti	20	1	<1	1	<1	<1	<1	<1

Table C-3. Analysis of early LiF crystals.

Date: 3-21-72

	A	B ₁	B ₂	C	
Al	300	30	500	100	Key: Numbers = Approximate ppm by wt
Ca	3	20	100	30	
Cu		1	3		Sample Description: LiF Crystals
Fe		30	30		
Mg		30	10		A. - Boil off
Mn		3	10		B. - Crud - Top Melt
Ni	10	200	3000	200	B ₁ - White
Si		10	10		B ₂ - Dirty
Ti		30	30		C. Bottom Melt

SPECTROCHEMICAL ANALYSIS REPORT
LRL - LIVERMORE -- ANALYTICAL LABORATORY

Sample Description: LiF, Host Crystal 1)		Plate No.: 3073
		Sample No.: SS-0775
		Submitted By: R. Kloepping
		Date Received: 4-13-73 Date Reported: 4-25-73
		Analyst: E. Peck

Key:

Values are approximate ppm by weight for the elements requested.

Analysis:

Ti: Equal to or less than 1 ppm

Ti: Not detected, less than 3 ppm

Cu: 3 ppm

Ci: 4 ppm

APPENDIX D

"BASIC" COMPUTER PROGRAM FOR EVALUATION OF CRYSTAL
RESPONSE DATA AND PRINTOUT OF THE RESULTS

LIST

```

5 CLOSE 1
10 DIMS(255),B(255),X(255),Y(255)
20 PRINT "THIS PROGRAM IS FOR 250 DATA POINTS FROM A 256 CHANNEL SPECTRUM"
30 PRINT:PRINT "PLACE SIGNAL TAPE INTO READER THEN TYPE CR TO CONTINUE"
40 INPUT T
45 OPEN PR,1
50 FOR I=0 TO 250
55 INPUT #1,MFA,S(I)
60 NEXT I
65 PRINT:PRINT "PLACE TAPE TO BE SUBTRACTED FROM FIRST TAPE INTO"
70 PRINT "READER AND TYPE CR TO CONTINUE":PRINT
73 CLOSE 1
75 INPUT T
77 OPEN PR,1
80 FOR I=1 TO 250
85 INPUT #1,MFA,B(I)
90 NEXT I
95 CLOSE 1
100 PRINT:PRINT:PRINT "CALCULATIONS ARE NOW IN PROGRESS PLEASE BE PATIENT!"
110 PRINT:PRINT:PRINT
120 FOR I=1 TO 250
130 LET X(I)=S(I)-B(I)
140 NEXT I
150 FOR I=1 TO 250
160 IF S(I)>0 THEN 180
170 LET S(I)=1
180 IF B(I)>0 THEN 200
190 LET B(I)=1
200 IF X(I)>0 THEN 220
210 LET X(I)=1
220 NEXT I
270 LET S=0
280 LET B=0
290 LET X=0
300 FOR I=1 TO 250
310 LET S=S+S(I)
320 LET B=B+B(I)
330 LET X=X+X(I)
340 NEXT I
350 GOSUB 5100
360 PRINT:PRINT:PRINT
400 PRINT:PRINT:PRINT "OKAY WE ARE NOW READY TO PLOT THE DATA"
405 LET Q=X
410 PRINT "PLACE PEN AT 0,0 AND TYPE CR TO CONTINUE":PRINT:PRINT
411 PLT:
412 PEN0
413 PLOT 0,0
414 INPUT T

```

```

415 PASHY:829
417 PRINT "THAT WAS A PLOT OF THE SIG-BKGD, DO YOU ALSO WANT"
418 INPUT Y
419 GOTO 7500
420 PLY:
430 PEN0
440 PLOT 0,0
470 PAGE
480 MODE 0
490 PLOT 100,100
500 PEN1
510 FOR I=1 TO 250
530 PLOT 100+X, 6*I, (-50)+150*Y(I)
540 NEXT I
550 PEN0
560 PLOT 1000,100
570 PEN1
580 PLOT 100,100
590 PLOT 100,1000
600 PEN0
610 LABEL 100,2,4,1,"CHANNEL NUMBER"
620 LABEL 40,100,4,0,"COUNTS PER CHANNEL"
630 PEN0
640 PLOT 100,100
650 FOR I=1 TO 6
660 PLOT 90,100+150*I,4,2,6
662 LABEL 25,90+150*I,2,1,10
663 LABEL 64,10+150*I,1,1,1
670 NEXT I
680 FOR I=1 TO 25
690 PLOT 100+X, 6*10*I,90,6,1,6
691 IF I*10=50 THEN 900
692 IF I*10=100 THEN 920
693 IF I*10=150 THEN 940
694 IF I*10=200 THEN 960
695 IF I*10=250 THEN 980
696 REM RETURNS HERE
700 NEXT I
703 PRINT "TOTAL COUNTS INTEGRATED FROM CHANNELS 1 TO 250 : "0
710 RETURN
900 LABEL 90+X, 6*50,70,1,1,"50"
905 PLOT 100+X, 6*1*10,90,10,1,6
910 GOTO 692
920 LABEL 85+X, 6*100,70,1,1,"100"
925 PLOT 100+X, 6*1*10,90,10,1,6
930 GOTO 693
940 LABEL 85+X, 6*150,70,1,1,"150"
945 PLOT 100+X, 6*1*10,90,10,1,6
950 GOTO 694
960 LABEL 85+X, 6*200,70,1,1,"200"

```

```

965 PLOT 100+X.6*1*10,90,10,1,6
970 GOTO 695
980 LABEL 85+X.6*250,70,1,1,"250"
985 PLOT 100+X.6*1*10,90,10,1,6
990 GOTO 696
1100 PRINT:PRINT "CALCULATIONS ARE IN PROGRESS PLEASE BE PATIENT"
1105 FOR I=1 TO 250
1110 LET Y(I)=S(I)
1115 NEXT I
1120 FOR J=1 TO 250
1130 LET Y(J)=LOG(Y(J))/LOG(10)
1142 IF Y(J)>1 THEN 1150
1144 LET Y(J)=1
1150 NEXT J
1160 LET Q=S
1170 GOSUB 420
1175 PRINT:PRINT "AGAIN CALCULATIONS ARE IN PROGRESS PLEASE BE PATIENT"
1180 GOTO 2100
2100 FOR K=1 TO 250
2110 LET Y(K)=E(K)
2120 NEXT K
2130 FOR L=1 TO 250
2140 LET Y(L)=LOG(Y(L))/LOG(10)
2142 IF Y(L)>1 THEN 2150
2144 LET Y(L)=1
2150 NEXT L
2160 LET Q=E
2170 GOSUB 420
2180 PAGE
2190 GOTO 7100
5100 FOR I=1 TO 250
5110 LET Y(I)=LOG(X(I))/LOG(10)
5112 IF Y(I)>1 THEN 5120
5114 LET Y(I)=1
5120 NEXT I
5130 RETURN
7100 PRINT:PRINT:PRINT:PRINT "          ALL DONE"
7110 PRINT:PRINT:PRINT "MORE DATA TYPE 1, NONE TYPE 0"
7120 INPUT I
7130 IF I>0 THEN 30
7140 FOR J=1 TO 50
7150 PRINT
7160 NEXT J
7171 END
7500 IF I=0 THEN 7100
7510 IF I=1 THEN 1100
7520 GOTO 410
READY

```

APPENDIX E
PHOTON SOURCE DATA

Source data					
Source	Original content (μ Ci)	Date of calibration	$T_{1/2}$	t	Content at time of experiment (μ Curie)
^{109}Cd	118.9	1-11-72	453d	155d	93.8
^{241}Am	11.3	16-2-73	458y	47d	11.3
^{203}Hg	11.0	16-2-73	46d	47d	5.49
^{137}Cs	11.3	16-2-73	30y	46d	11.27
^{54}Mn	11.9	16-2-73	312d	48d	10.70
^{60}Co	13.5	16-2-73	5.258y	48d	13.27

APPENDIX F

THEORETICAL MODEL FOR THE SCINTILLATION PROCESS

Introduction

The luminescence of inorganic crystals is generally a crystalline property inherent to the host lattice and activator ions. Usually, the luminescence is due to the presence of small concentrations of specific impurities in the host crystal. Certain properties of the phosphors are important to the scintillation mechanism, namely: (1) the scintillation efficiency, (2) emission and absorption spectra, (3) response as a function of the incoming energy deposited through a specific distance traveled in the crystal, (4) the scintillation decay components, and (5) the decay time of the fast component. All five of these properties are dependent upon the nature of the crystal, the nature and concentration of the activator, and the temperature.

The scintillation process is hypothesized to be due to the following contingent sequence of events which can occur in a hypothetical crystal of an alkali halide activated when a photon interacts with it:

1. The production of electron-hole pairs by ionization by means of:
 - (a) Compton scattering and absorption,
 - (b) photoelectric absorption, or
 - (c) pair production.

All three of these mechanisms are defined in terms which are functions of the photon energy and the atomic number.

2. The electron-hole pairs may either diffuse through the crystal or recombine to form excitons (a bound electron-hole pair).
3. The electron-hole pairs or excitons may be captured by lattice traps.
4. The electron-hole pairs may continue to diffuse (binary diffusion) in the conduction and valence bands respectively as the excitons may migrate (nonradiatively) until process 5 or 6 occurs.
5. The electron-hole pair or excitons may be captured by a luminescence center.
6. The electron-hole pair or excitons may be captured by a quenching center.
7. The capture by a luminescence center (normally the activator ion) results in thermal activation to a higher energy state and then decay with the emission of a photon.

Specific alkali halides have been extensively studied, and the empirical results have been compiled to fit various theoretical models.¹ The general mechanisms first proposed (Refs. 1, 37, 56) are still good first-order approximations. A general scintillation model given by Birks will be followed in the review and discussion in this Appendix. This review will also encompass the basic theory on the interaction of radiation with matter.

Classical Mechanisms of Photon Interaction with Matter

When a photon interacts with matter, it first forms electron-hole pairs by ionization. It is observed experimentally in these

interactions that the intensity of the interacting photon as it passes through matter decreases, as described in the following equation:

$$-\frac{dI}{dx} = \mu I \quad (F-1)$$

where

$\frac{dI}{dx}$ = rate change in intensity of the interacting photon I

with distance x, and

μ is a proportionality constant called the attenuation coefficient.

The integral equation in a uniform radiation field is

$$I = I_0 e^{-\mu x} \quad (F-2)$$

where

I_0 = the initial intensity.

The attenuation coefficient μ is the sum of the three interactions¹ which carry the notation σ (total Compton cross section), τ (photo-electric cross section), and κ (pair-production cross section).

Therefore, Eq. (F-1) may be defined as:

$$dI = -(\sigma + \tau + \kappa) I dx. \quad (F-3)$$

Since the total coefficient is a sum, each of the individual processes may be discussed individually in detail. Since this dissertation considers photon energies from 20 keV to 2 MeV, all of these photon interactions occur, although the contribution from pair production is insignificant.

Compton Effect

The dominant photon interaction in the energy region, nominally between 0.5 and 5 MeV, is Compton scattering.⁷² The Compton effect occurs when a photon is scattered with a change in direction and a decrease in energy, while the electron recoils with the remainder of the photon energy. The energy of the incident photon is divided between the scattered photon and the electron, as illustrated in Fig. F-1. The energy of the scattered photon is given by

$$E' = \frac{E}{1 + \alpha (1 - \cos \theta)} \quad (\text{F-4})$$

and the kinetic energy of the recoil electron is given by

$$T_c = E - E' \quad (\text{F-5})$$

$$T_c = \frac{\alpha E (1 - \cos \theta)}{1 + \alpha (1 - \cos \theta)} \quad (\text{F-6})$$

where

$E = h\nu$ (the energy of the incident photon),

$\alpha = h\nu/mc^2$,

θ = the scattering angle (see Fig. F-1).

The cross section for Compton scattering over the energy range 0.5 to 5 MeV is calculated by the Klein-Nishina equations.⁷³ The equations are based on a quantum mechanical approach using the Dirac notation to describe the free electron to show the fractional energy scattered and absorbed. The total Compton cross section is given by the following equation:⁷⁴

Fig. F-1. Compton effect.

$$e^{\sigma} = 2 \pi r_o^2 \left\{ \frac{1 + \alpha}{\alpha^2} \left[\frac{2(1 + \alpha)}{1 + 2\alpha} - \frac{1}{\alpha} \ln(1 + 2\alpha) \right] + \frac{1}{2\alpha} \ln(1 + 2\alpha) - \frac{1 + 3\alpha}{(1 + 2\alpha)^2} \right\} \quad (F-7)$$

where

r_o = the classical electron radius and all other variables are previously defined.

The scattering cross section is derived in a similar manner:⁷⁵

$$e^{\sigma}_s = \pi r_o^2 \left[\frac{1}{\alpha^2} \ln(1 + 2\alpha) + \frac{2(1 + \alpha)(2\alpha^2 - 2\alpha - 1)}{\alpha^2 (1 + 2\alpha)^2} + \frac{8\alpha^2}{3(1 + 2\alpha)^3} \right]. \quad (F-8)$$

Therefore, the cross section for the energy absorbed is related by the following:

$$e^{\sigma} = e^{\sigma}_s + e^{\sigma}_a. \quad (F-9)$$

For the total removal of the photons incident on a detector, the use of the total Compton cross section e^{σ} is required. Published values will be used when discussing attenuation as used in Eq. (2), and for the theoretical energy response of LiF given in Appendix A. The published values of McMaster⁷⁵ will also be used to evaluate LiF by Eq. (2).

The Compton mass attenuation coefficient can then be given by Eq. (F-10) since

$$\sigma / \rho = N_O (Z/A) e^6 \quad (F-10)$$

where

N_O = Avogrado's number,

Z = the atomic number,

A = the atomic weight,

ρ = the density.

It has been shown¹ that σ / ρ is nearly independent of the nature of the absorber, and $Z/A \approx 0.45$ for all elements except hydrogen. The values σ / ρ are applicable to scintillators in general except organic scintillators. From the above relationship, the energy imparted by the incoming photons to the electrons can be computed for LiF crystals.

Photoelectric Effect

The photoelectric effect is where the incoming photon imparts all of its energy to a bound electron. The bound electron utilizes part of the energy to neutralize the binding energy and the remainder appears as kinetic energy, a dominant mechanism for low photon energies. Theoretical analysis of the photoelectric processes are very difficult since they require that relativistic equations, derived by Dirac, be used to describe a bound electron in the calculations. Based on the works of several experimenters,⁷⁶⁻⁸¹ it is convenient to divide the photoelectric effect into three energy ranges of less than 0.35 MeV, 0.35 to 2 MeV, and those greater than 2 MeV. Only the first two are pertinent to this dissertation.

Hulme et al.⁷⁶ did the major work in calculating the photoelectric cross sections in the energy range 0.35 to 2 MeV. The calculations were

based on the following assumptions: (1) the exchange interactions between atomic electrons are neglected, (2) each K electron is treated separately, (3) the system considered has only one nucleus and one K electron, and (4) the result of the calculations can be doubled to give a first approximation of the total K-shell absorption.

The model can be expressed as a perturbation of the K electron by photons traveling along a Z reference axis.

The resultant perturbation on the K electron is its absorption of a quantum of energy and a jump to the free state as a photoelectron.

The integration of the relativistic wave equation can be rigorously approximated; the results are given by Hulme *et al.*⁷⁶ The values obtained by Hulme are in agreement with both Hall⁷⁷ and Sauter⁸⁰ to $\pm 10\%$ for photon energies above 1 keV and below 1 MeV respectively.

The equation for the absorption cross section of the K shell used by Hall for energies greater than 2 MeV is:

$$\sigma_K = \frac{(3/2)\theta_0 (1/137)^4 Z^5 n}{\eta^2 \eta'^2 e^{\eta(\pi-2\eta)}} \left\{ \kappa'_0{}^3 \epsilon n^4 \left[\frac{4}{3\epsilon} + \frac{\epsilon-2}{\epsilon+1} \right] \right. \\ \left. \times \left(1 + \frac{1}{2\epsilon\kappa'_0} \ln \frac{\epsilon - \kappa'_0}{\epsilon + \kappa'_0} \right) \right\} \quad (F-11)$$

where

Z = the atomic number,

$n = mc^2/h\nu$,

$137 = hc/2\pi e^2$,

$\theta = 8\pi r_a^2/3$,

$\eta = Z/137$,

$$\epsilon = (1/n) + (1 + \eta^2),$$

$$\kappa'_0 = (\epsilon^2 - 1)^{1/2}.$$

$${}_a\tau_\kappa = \text{photoelectric absorption coefficient in cm}^2/\text{atom}.$$

To account for the interactions of the outer shells by the equations presented by Stobbe⁸¹ and Hall,⁸² the results can be brought into approximate agreement with experimental results by multiplying by 5/4. An empirical formula appears in a dissertation by Crites⁸³ in which the total cross section is given in Eq. (F-12).

$${}_a\tau = \tau_\kappa (1 + 0.01481 \ln^2 Z - 0.000788 \ln^3 Z) \quad (\text{F-12})$$

where

${}_a\tau$ represents the true absorption; (that is the conversion of the interacting photons into the kinetic energy of a photoelectron).

The equation used generally for energies between 0.1 and 0.35 MeV is given by Sauters:⁸⁰

$${}_a\tau_\kappa = 3/2 \phi_0 \frac{Z^5}{(137)^4} n^5 (\gamma^2 - 1)^{3/2} \left[4/3 + \frac{\gamma(\gamma - 2)}{\gamma + 1} \right. \\ \left. \times \left(1 - \frac{1}{2\gamma(\gamma^2 - 1)^{1/2}} \ln \frac{\gamma + (\gamma^2 - 1)^{1/2}}{\gamma - (\gamma^2 - 1)^{1/2}} \right) \right] \quad (\text{F-13})$$

where

$$\gamma = \frac{1}{(1 - \beta^2)^{1/2}} = \frac{h\nu - E_B + mc^2}{mc^2}.$$

E_B = the binding energy of a K electron. All other symbols are defined in equations previously given.

Victoreen⁸⁴ developed an empirical equation for the photoelectric absorption coefficients in the energy range between 1 keV and 1 MeV. This is in good agreement with the results of Hulme,⁷⁸ particularly in the region of low Z . It should be noted that in this low-energy region (below ~ 100 keV) absorption edges form discontinuities in cross-section formulas. Such a discontinuity results when the photon energy becomes less than the binding energy of some of the electrons. Therefore, the number of electrons with which the photon can interact to eject a photoelectron is reduced sharply. The result is a sharp decrease in a_{κ}^7 as a function of E . The detector phosphor of a high- Z material may have high detector efficiencies but poor linear energy response. This property is one of the major factors in selecting low LiF as the lattice host to obtain the desirable linear energy response. This is substantiated in the equation of Hulme,⁷⁸ Hall⁷⁷ and Sauter⁸⁰ where a_{κ}^7 is a function of Z with an exponent of 4 to 5.

Pair Production

Pair production is the conversion of the photon energy, reacting with the field of the nucleus, into a positron and electron, each with the same mass. The remaining photon energy above 1.02 MeV goes into the kinetic energy of the two particles. The theoretical analysis was first made by Bethe and Heitler,⁸⁵ and later by Jaeger and Hulme.⁸⁶ Bethe and Heitler used the Born approximation, where the interaction of electron and nucleus may be considered as only a small perturbation, to obtain the cross section for pair production. Their equation for the cross section limits the total energy between E_+ and $E_+ + dE$ and E_- and $E_- + dE_-$ for positrons and electrons, respectively. The pair-production cross section is defined in terms of Z and E by

$$a^k = (Z^2/137)(e^2/m_0c^2)^2. \quad (F-14)$$

Energy Transport

The basic scintillation processes 2, 3, 4, 5, and 6 described in the Introduction to this Appendix are grouped together in this section since the sum of these processes describes how energy moves from the site of interaction to the color center.

The process of exciton formation (2) is described in articles by Murray and Meyer,³⁶ Williams,⁸⁷ Van Sciver,⁸⁸ and others. These authors agree that the luminescence caused by radiation is the end result of the color center (e.g., Tl^+ ion) (1) being excited from the ground state by the absorption of energy (excitons or electron-hole pairs) to the excited state, and (2) decaying back to the ground state with the loss of energy as light. The excitation of the Tl^+ ion center is described in experiments by Kaifu and Tomura,⁸⁹ and by Harlan and Wilt, reported in Ref. 90. These experiments indicate that excitation is the result of an energy transport of excitons, or independent binary diffusion of electrons and holes from the path of the incident gamma photon to the Tl^+ ion site. The carriers must have a net charge of zero to retain the charge state of the Tl^+ ion. Once the center is excited, it may decay by emission of a photon or by nonradiative transitions.

A detailed model for the process described has been proposed by Murray and Meyer.³⁶ They made the following assumptions and definitions as a basis for their model: (1) each activator site and lattice defect site can capture only one exciton for each given incident photon; (2) almost all of the energy loss of the incoming photon produces ionization; (3) the number of ion pairs per unit path length

is directly proportional to dE/dx ; (4) the excitons diffuse radially from the ionization path and can be mathematically described in cylindrical geometry; and (5) a thin crystal section normal to the path of the incident gamma photon will define the boundary condition. Based on the assumptions stated, Murray and Meyer³⁶ equated process 2 as follows:

$$\frac{n_o}{n_e} = \frac{\alpha n_e}{1 + \alpha n_e} = \frac{\alpha K(dE/dx)}{1 + \alpha K(dE/dx)} \quad (F-15)$$

where

n_e = the initial number of free electrons or holes,

n_o = the number of excitons formed,

$\alpha = k_r/k_T N_T$

k_r and k_T = constants,

N_T = the trap density,

$K = n_e/(dE/dx)$.

Given that the electrons and holes are displaced with the larger ions remaining in a relatively fixed state, the exciton diffusion process was then defined by Murray and Meyer as:

$$\frac{1}{v} \frac{\partial n}{\partial t} = Dv^{-2} - n(N_e \sigma_e + N_a \sigma_a) \quad (F-16)$$

where

n = the density of free carriers,

v = the velocity of the carriers,

D = a constant (with dimensions in cm),

N_a = the density of unoccupied activator sites,

N_e = the density of the traps,

σ_a = the site capture cross section,

σ_e = the trap capture cross section.

The density term N_e was evaluated as approximately 10^3 times $N_a \cdot N_a$ at time 0, and is defined as N_a^0 .

The expression was evaluated and the results used to express an equation defining the scintillation efficiency of a phosphor dL/dE as

$$dL/dE = \frac{1}{\epsilon} (n_o/n_e) S P_L P_e \quad (F-17)$$

where

n_o/n_e is as previously defined in Eq. (F-16),

E = the energy loss of a photon required to produce an ion pair, approximately 10 eV,

S = the number of activator sites which capture an exciton per initial exciton,

P_L = the probability of radiative transitions of the activator site,

P_e = the concentration quenching parameter.

Values for S were determined,³⁶ and it was shown that P_L and P_e were numbers of the order of unity. Thus, the efficiency of the processes of exciton formation, initial photon energy transfer to the excitons, and carrier diffusion energy transport to the activator sites can be evaluated, and this efficiency is termed detector phosphor efficiency. The calculations by Murray and Meyers were based upon a sodium iodide host lattice with thallium as an activator site. The basic transport mechanisms they describe should be applicable also to LiF

doped with Tl. The values derived are obviously different for LiF (Ti), and will require evaluation.

Birks¹ expressed dL/dE as equivalent to

$$\frac{dL}{dE} = \frac{1}{E_{wx}} \left(\frac{n_o}{n_e} \right) f'_{xy} q_{oy} \quad (F-18)$$

where

n_o/n_e is as previously defined in Eq. (F-15),

q_{oy} = a term which includes the effect of the concentration of a quenching parameter,

f'_{xy} = the quantum efficiency of energy transfer from lattice to the activator ion, and

$$f_{xy} = \frac{(\sigma_a/\sigma_e)[Y]}{1 + (\sigma_a/\sigma_e)[Y]} \quad (F-19)$$

where

$f_{xy} = f'_{xy}$ when dE/dx is less than $20 \text{ keV me}^{-1} \text{ cm}$,

$[Y]$ = the activator concentration,

σ_a = the color center capture cross section,

σ_e = the capture cross section for trap sites.

Birks has obtained empirical data for f'_{xy} values, and did not derive a formal mathematical expression for it. Recent work by Ladu *et al.*⁵⁸ similarly expresses the equation for dL/dE , but with some modification and a difference of opinion as to the exact nature of the mechanisms. The end result appears to be in agreement both with the models of Murray and Meyer, Birks, and other experimental evidence.

Quantum Theory of Excitation and Decay of Impurity Centers

Once the energy has been absorbed by a thallium or similar impurity site, the ion is excited and then decays followed by emission of a photon. This process is best described in quantum mechanical and crystal field notation for both crystal and impurity sites. The quantum mechanical description of the crystal and of the impurity sites for several alkali halides are given in Refs. 31, 32, 33, and 55. From the quantitative values obtained, two important properties can be theoretically derived for the phosphor; namely, (1) the half life (decay time) of the center, and (2) spectra (emission) which can then be matched to the proper photomultiplier tube. The specific theoretical calculations for LiF (Tl) and LiF (Ti) are beyond the scope of this study.

Williams⁵⁵ was one of the first to attempt a quantitative interpretation of solid-state luminescence. He proposed that the most probable sites responsible for absorption and emission spectra were the activator sites. Tl was the activator, and he derived the theoretical spectrum for the crystal from the free Tl^+ ion spectrum and from quantum selection rules. The ground state for the Tl^+ ion is $6s^2, {}^1S_0$, and the lowest excited state is $6s, 6p$, which consists of three triplet states ${}^3P_0, {}^3P_1$ and 3P_2 and a singlet 1P_1 . The coupling for Tl^+ ion is not pure LS but is part JJ, and the multiplicity selection rule $\Delta S = 0$ is not enforced. The selection rules hold for parity, angular orbital momentum $\Delta L = \pm 1$ and for total angular momentum $\Delta J = 0 \pm 1$ except when $J = 0 \rightarrow J' = 0$.

The substitution of small quantities of Tl^+ for Li^+ in LiF produces localized distortion in the lattice. The 1S_0 Tl^+ ion (spherically symmetrical) has different properties than the Li^+ ion: (1) ionic radius r_0 , (2) polarizability α , (3) exponential variations of repulsion energy, and (4) overlap integrals. Previous published data⁵⁵ using KCl as the host showed the σ nearest Cl^- neighbors to be equally displaced. The ionic radius of the K^+ ion is $1.33\text{\AA}$, Cl^- ion is $1.81\text{\AA}$, Tl^+ ion is $1.51\text{\AA}$, Ti^{2+} ion is $0.90\text{\AA}$ and with Li^+ ion as $0.68\text{\AA}$ and F as $1.33\text{\AA}$ it can be seen the displacement with Tl^+ and even Ti in the LiF will be large compared to KCl . This may account for the difficulty in doping LiF with large cations. Williams has shown that the absorption occurs according to the Frank-Condon principle. Therefore, the transition from 1S_0 to a $^3P_1^0$ state occurs with retention of the configurational properties of the 1S_0 state. After absorption and promotion to the $^3P_1^0$ state, the $^3P_1^0$ state will come to thermal equilibrium with the lattice because the lifetime of the excited state is long compared to the period of lattice vibration. The emission process may be regarded as the reverse of the absorption process governed under the same principles. The values of r_0 (ionic radius), α (polarizability) and P (repulsion energy) for both the 1S_0 Tl^+ and the $^3P_1^0$ Tl^+ state can be evaluated using Hartree self-constant field theory for $6s^2$, $6s$, $6p$. Therefore, the changes in the total energy of the system can be calculated as functions of the displacement Δa and $\Delta a'$ of the crystal lattice as defined by Williams. Although these values have been reported by Williams for KCl (Tl^+) only, the general theory should be applicable to other alkali halide crystals.

Williams solved the various equations required to determine the values previously described for the Tl^+ ions. He calculated the change in total energy for the system. The energy E for $^1S_0 Tl^+$ and E' for $^3P_1^0 Tl^+$ ion was determined as a function of Δa and $\Delta a'$. The changes in van der Waals energy was computed for KCl (Tl) by Mayer.⁹¹ From the data, the lattice energies for the $^3P_1^0$ and 1S_0 states are calculated as functions Δa and $\Delta a'$. The theoretical absorption and emission spectra can then be calculated from the total energy change,

$$\Delta E = E' - E. \quad (F-20)$$

The emission spectrum was a probability function of the transition energy ΔE and was given as

$$P'(\Delta E) = C' \exp \{ (E' - E_0) / kT \} d(\Delta a / d\Delta E) \quad (F-21)$$

where

C' = a normalization constant,

E'_0 = minimum energy of the state,

k = the Boltzman constant,

T = the absolute temperature,

Δa = is previously defined,

E' = is previously defined.

The work by Williams demonstrates that the major luminescent properties of alkali-halide activated crystals can be derived quantitatively from theory. His detailed calculations also provide an insight into what occurs in the LiF crystal structure.

The experimental evidence and theoretical models of Williams were compared to research reported by Potekhina⁹² in the evaluation of $4d^{10}$, $4d^9 5p Ag^+$ ion states. The results of the $4d^{10} \rightarrow 4d^9 4s$ transition compare favorably with the method of Williams. However, Potekhina noted that the $4d^{10} \rightarrow 4d^9 4p$ transition is the more likely transition leading to the emission spectrum observed. The method of Potekhina is more rigorous and takes into account better approximations of the forces and revised quantum theory of lattice energies.

Consistent with Williams' work, the emission spectra of Ti^{2+} activated LiF should result from the decay of an excited Ti^{2+} state to its ground state. Ti^{2+} ion being in the first transition series, the selection rules will be more rigorously enforced. The Ti^{2+} is of d^2 configuration and has a free ion ground state 3F_2 with an allowed transition to $^3P_{0,1,2}$ excited states and the emission spectrum resulting from the decay from a 3P level to the 3F ground state. The theoretical calculations for determination of the emission spectrum for Ti^{2+} were not made.

It has been reported that Ti^{4+} , d^0 configuration is the ionic species present in most LiF crystals. The ground state would be 1S_0 . However, it may be more appropriate to consider the molecular state (σ) since the atomic P-level electrons require considerable promotion energy.

Summary

Gamma photons are attenuated and absorbed by three different processes: (1) photoelectric, (2) Compton effect, and (3) pair production. These processes are important over three general energy regions, and may shift somewhat as a function of Z. At the very low energies the

absorption by the photoelectric mechanism dominates, but for low-Z material the photoelectric effect, because it is a general function of Z^{4-5} , is considered negligible below 100 keV. In the range from 100 keV to 4 MeV, the Compton effect is the most important means of absorption. Pair production begins at 1.02 MeV and although the other mechanisms are decreasing in effect, its contribution is still minor for low-Z material and below energies of 4 MeV. The total absorption (attenuation) coefficients can be calculated from the individual mechanism. Previously calculated coefficients are used in Appendix A and Appendix B for calculating the energy dependence of LiF (Ti). By ionization, the incoming photons are converted to electron-hole pairs.

The absorption of energy in the phosphor of thickness, d , can be represented as the sum of the previously calculated interaction cross sections,

$$e^{\sigma}, a^{\tau}, a^{\kappa}$$

$$f = 1 - e^{-\mu} \quad (F-22)$$

where

$$\mu = \tau + \sigma + \kappa,$$

μ = The attenuation coefficient,

σ = the total Compton cross section,

a^{τ} = the photoelectric absorption cross section,

a^{κ} is defined as the pair production absorption coefficient,

a^{μ} is related to e^{σ} , a^{τ} , a^{κ} and is the absorption coefficient.

The absolute scintillation efficiency, which is a true comparison of scintillator phosphors, is described by

$$S_Y = \frac{E_{py}}{E_{wx}} \left(\frac{n_o}{n_e} \right) (f_{xy})(q_{oy}) \quad (F-23)$$

where

E_{py} = the photon energy,

E_{wx} = the energy loss required to produce an electron-hole pair,

n_o/n_e is defined by Eq. (F-15),

f_{xy} and q_{oy} are defined by Eqs. (F-19) and (F-20).

The luminescence may be ascribed to the Ti^{+} ion transition $^1S_0 \rightarrow ^3P_1 \rightarrow ^1S_0$ and the Ag^{+} transition to $^1S_0 \rightarrow ^3P_0$, or 1P_1 or 3D_1 which are permitted by selection rules. The luminescence of LiF (Ti^{2+}) crystal can possibly be ascribed to the $Ti^{+2} d^2$ configuration transitions $^3F_2 \rightarrow ^3P_{0,1,2} \rightarrow ^3F$. The theoretical calculations are not presented in this work. Likewise, it must be stated that Ti probably can exist in the +4 state with a 1S_0 or $^1\sigma$ ground state.

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