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THEORETICAL AND PRACTICAL IMPLICATIONS OF THE EFFECTS
OF TEMPERATURE DURING IRRADIATION AND DURING
PRE- AND POST-IRRADIATION STORAGE ON THE RESPONSE
OF THERMOLUMINESCENCE DOSIMETERS

By
E. Gail de Planque

January 1984

Environmental Measurements Laboratory
New York, New York

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ABSTRACT

Experiments have been conducted to determine the applicability of the Randall-Wilkins theory for describing the behavior of $\text{CaF}_2:\text{Mn}$ thermoluminescence dosimeters (Harshaw TLD-400 chips). Results were obtained for four different conditions: irradiation followed by storage, irradiation after storage, irradiation both preceded and followed by storage, and continuous simultaneous irradiation and storage. The experiments were performed for storage intervals of approximately 1, 2, 3, 5, 6 and 7 days at five different storage temperatures: -25 , $+20$, $+65$, $+150$ and $+175^\circ\text{C}$. The results indicate fading that is described not by the Randall-Wilkins theory but rather as a linear function of the logarithm of the storage time. While the results suggest that the trapping efficiency is independent of temperature, they do demonstrate a small decrease in TL response with storage time prior to irradiation which is independent of temperature and time (>17 hours) and hence probably not dosimetric in origin but perhaps optically related. Glow curve analyses support the concept of a band of traps rather than a single trap. The overall results are compared to other data available in

the literature most of which is for room-temperature storage. These data, for storage periods ranging from minutes to one year, can also be described as a linear function of the logarithm of the storage time and are remarkably consistent when uniformly normalized. Although peripheral experiments revealed problems associated with self-irradiation as well as a decline in sensitivity with use, the stability experiment results verify the highly favorable stability properties of $\text{CaF}_2:\text{Mn}$ for widespread application.

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I. INTRODUCTION

A. Brief History of Thermoluminescence Dosimetry

While the direct association of the phenomenon of thermoluminescence with ionizing radiation was reported as far back as the turn of the century by investigators such as Wiedemann and Schmidt (1895) and Curie (Del Vecchio, translation, 1961), the application to radiation dosimetry really began in the late 1940's, particularly with investigations of Farrington Daniels and his colleagues at the University of Wisconsin as described by the historical accounts of Daniels (1967) and Schulman (1967). Early usage occurred primarily in the fields of medical and personnel dosimetry. Research efforts were concentrated upon the phenomenon itself along with the development of readout instrumentation, thermoluminescence detectors and procedures that would provide practical and reliable dosimetry for these applications.

In the 1960's and 1970's, thermoluminescence dosimetry made impressive inroads in clinical, personnel and environmental dosimetry as well as in more exotic applications (Cameron et al., 1968; Becker, 1973; Oberhofer and Scharmann, 1981). Clinical usage ranged from the determination of doses received during radiodiagnostics and radiotherapy (Roswit et al., 1970; Ruden, 1971; Gooden and Brukner, 1971; Parker et al., 1972; and Harley et al., 1976) to nationwide surveys of the accuracy of teletherapy units (Soares and Ehrlich, 1978).

Personnel dosimetry, probably the major field of application, has grown continuously (Attix, 1972 and Becker, 1976) to the point that today over 70,000 TLD personnel monitoring badges are processed per month in

the United States alone (excluding military personnel) using commercial systems and about three times that are used internationally. Some of the more innovative early applications have been in the ''gray'' area where personnel and environmental dosimetry meet. For example, in 1964, Cullen (1966) distributed TLD's enclosed in a religious medal, designed to be worn around the neck, to individuals in the high radiation background monazite zone of Brazil to assess population doses over a three-month interval. With a different thrust, Lucas and French (1967) used TLD's in a radioecology study at a twenty acre desert site irradiated with ^{137}Cs to investigate environmental dose profiles as well as the dose to the rodent and lizard population.

The use of TLD's for environmental monitoring began in the mid 1960's (see the historical account of de Planque and Gesell, 1982). For example, in 1965, a TLD system was put into operation for monitoring gamma radiation exposure in the off-site environment surrounding the Nevada Test Site (Fitzsimmons and Horn, 1969), and about one year later, TLD's were incorporated into the environmental surveillance network, including over 300 stations, at the Atomic Energy Commission's National Reactor Testing Station in Idaho, an 898 square mile complex (Cusimano et al., 1968a, 1968b). By the early 1970's, programs emerged involving the use of TLD's for measuring variations in the natural radiation environment (Burke, 1972a) including the simultaneous measurement of the environmental radiation background at 107 weather stations throughout the United States (Lindeken et al., 1972). A more recent study of this type with TLD's was of a high background area in the People's Republic of

China and consequent health effects (High Background Radiation Research Group, China, 1980). Today, one or more TLD monitoring networks is in place around every operating nuclear power plant and most nuclear facilities in the United States (Conti, 1978, Slobodien, 1980 and, Mattson et al., 1980) and around many if not most analogous facilities in the rest of the world. In fact the assessments of the population dose and health impact of the accident at the Three Mile Island Nuclear Power Plant were based largely on environmental TLD measurements (Battist et al., 1979). The extent of current interest in TLD's for environmental measurements is reflected by the participation of over 100 laboratories representing 27 countries in the 1982 series of voluntary intercomparison studies of environmental dosimeters begun in the mid 1970's (Gesell et al., 1976; de Planque and Gesell, 1979; Gesell et al., 1978; Gesell and de Planque, 1980).

In a different application, the thermoluminescence of roof tiles from Hiroshima was used to aid in the determination of doses from the atomic bomb (Higashimura et al., 1963 and 1967; Ichikawa et al., 1966). This technique is again under consideration for making re-estimates of these doses (Wrenn, 1982) as well as for the retrospective determination of doses to the Utah and Nevada populations from direct Nevada Test Site weapons fallout (Haskell et al., 1981; Haskell and Wrenn, 1983). In the latter case, material obtained from bricks is being used as the dosimetric material.

More exotic applications of the principle of thermoluminescence dosimetry have included the dating of numerous types of materials (for a useful bibliography see Wagner, 1981) including meteorites (Durrani and

Christodoulides, 1969), moon rocks (Hess et al., 1971), minerals (Hwang, 1970; Mejdahl, 1971), ancient pottery (Courtois et al., 1977; Francois et al., 1977; and Zimmerman, 1967) volcanic tuff (Wintle, 1982), Quaternary calcite (Wintle, 1978) and ocean sediments (Wintle and Huntley, 1979). Using similar principles, thermoluminescence dosimetry has also been used to detect fraudulent objets d'art (Aitken et al., 1971; Fleming et al., 1971).

In the space program, TLD's have been carried in several satellite flights (Schneider et al., 1972) as well as on the Apollo (Richmond and Lill, 1966) and Gemini (Richmond et al., 1966; Janni and Schneider, 1966) moon flights as a means of determining the radiation doses to astronauts. TLD's have also proven useful in providing dose estimates in radiation hardness testing of electronic components for nuclear weapons, missiles, and satellites (ANSI/ASTM, 1978).

Obviously much has been accomplished in the field of thermoluminescence dosimetry since the 1940's. Worldwide publications have been increasing at a rapid rate (Figure I-a) and standards concerning the performance and testing of environmental and personnel thermoluminescence dosimeters are now either in effect or in progress both nationally and internationally. (ANSI, 1975, 1981, 1982; Busuoli and Johns, 1980).

B. State-of-the-Art

In spite of the remarkable progress made in the application of thermoluminescence to problems of radiation dosimetry, knowledge of the physics of the processes involved must still be regarded as rather primitive. At this stage further improvements in the accuracy of TLD measure-

ments as well as further development and refinement of TLD instrumentation, techniques and materials are critically dependent on expanded knowledge of the physical processes involved.

The need for improved accurate dosimetry carries not only traditional scientific importance but enormous practical significance, especially for applications directed at the ultimate determination of radiation doses to people. In today's climate, accurate dosimetry has even social, economic and political importance as indicated by ongoing suits against the U. S. Government for health effects related to activities such as weapons testing and general public health concerns related to the peaceful uses of atomic energy, mainly nuclear power.

One particular aspect of thermoluminescence dosimetry critical to accuracy and still poorly understood is that of the stability of the dosimeter, over the period of use and under the temperature conditions prevailing during that period. Over the years, the general experience with instability problems has been in terms of "fading", i.e., the loss of stored signals, as reflected by the thermoluminescence (TL) response, after irradiation. However, more recent work indicates that instability also may take the form of sensitivity changes. Practically speaking, when these effects occur, radiation doses may be under or overestimated, unless proper corrections can be made. From the theoretical standpoint, these properties are at the heart of the thermoluminescence process and their study provides input for furthering the understanding of the physics of this phenomenon.

Thus, because of both the practical and the theoretical significance of the instability of thermoluminescence dosimeters, research on this subject has been undertaken.

Fig. I-a Approximate number of publications per year on thermoluminescence (TL) in LiF and in other materials, on radiophotoluminescence (RPL), track etching, and exoelectron emission. (After Scharmann, 1979, based on data by Attix, Fleischer, and Becker).

II. THEORY

Thermoluminescence dosimetry is based on the principle that the amount of light emitted from a thermally-stimulated dosimeter is proportional to the radiation dose absorbed by the dosimeter material during irradiation. As mentioned in Chapter I, there is still a great deal of speculation and controversy concerning the actual processes involved in the interaction of radiation with a TL phosphor and the consequent thermoluminescence processes. In a recent review of several of the complex schemes that have been proposed, Horowitz (1981) indicated that there are still 'no quantitative models which deal with the formidable complexity of the TL phenomenon. At best we have qualitative models dealing with average quantities and limited aspects of the problem'. While many models have been advanced, they all ultimately rely on the theory proposed by Randall and Wilkins in 1945, deriving their complexities from complicated manipulations and applications of the basic processes formulated by Randall and Wilkins.

The Randall-Wilkins theory is based on the ideas put forth in Appendix A which can be briefly and simply summarized as follows. Ionizing radiation excites an electron from the valence band to the conduction band of the TLD crystal leaving a hole in the valence band. The electron and hole move through the crystal until they are trapped in metastable states or 'traps' which are generally presumed to be associated with

crystal defects or impurity (usually dopant) sites. Upon thermal stimulation, sufficient energy is imparted to the trapped electron to enable it to escape from the trap and rise to the conduction band. The thermal activation energy, E , required to liberate the trapped electron is termed the trap depth. The electron then recombines with a hole at a luminescence center, emitting light in the process. As a dosimeter is heated, the probability of releasing the trapped electron is increased, and at some temperature T , for which the thermal activation energy equals that of the trap depth, there is a rapid increase in the release rate. A graph of the light emitted as a function of time or temperature is known as a glow curve.

Now, according to Randall and Wilkins (1945), the electrons in a trap have a Maxwellian distribution of thermal energies. If τ is the mean life time of a trapped electron and $1/\tau$ is equal to λ , the probability per unit time of a charge carrier escaping from a trap of depth E at temperature T , then

$$\lambda = s \exp (-E/kT) \quad 11-a$$

where k is Boltzmann's constant and s is the frequency factor assumed to be independent of temperature.

carriers once they have been trapped, i.e., once the radiation-induced signal has been stored. Assuming first order kinetics, they defined the change in the number of trapped charge carriers, n , in time t as,

$$\frac{dn}{dt} = -ns \exp (-E/kT) = -\lambda n \quad \text{II-b}$$

The procedure for producing a glow curve, commonly referred to as read-out, involves a deliberate thermal stimulation of the phosphor in which T increases with time t according to the relationship

$$dT = a dt$$

Then λ also varies with time and n is given by the equation

$$\begin{aligned} n &= n_0 \exp \left[- \int_0^t \lambda(t) dt \right] \\ &= n_0 \exp \left[- \int_{T_i}^T (s/a) \exp (-E/kT) dT \right] \end{aligned}$$

n_0 being the number of trapped charge carriers at time $t=0$, i.e., the beginning of readout, and T_i is the initial temperature during readout.

The TL response, which is proportional to the number of photons per second emitted during readout, at temperature T is given by

$$I(T) \propto n_0 s \exp(-E/kT) \exp \left[- \int_{T_i}^T s/a \exp(-E/kT) dT \right] \quad \text{II-c}$$

This is the Randall-Wilkins formula, and it along with the principle upon which it is based, equation II-a, form the basic elements of the Randall-Wilkins theory of thermoluminescence.

While this theory was used in early research mainly for investigating glow curves, it has been employed in more recent years to describe the processes taking place in the TLD phosphor prior to readout and is the most commonly accepted theory in this regard. Since the kinetics of the carrier population involves the trapping of charge carriers as well as their possible release, which depends on $\lambda(T)$, then equation II-b must be extended as follows:

$$\frac{dn}{dt} = \beta n_a - \lambda n \quad \text{II-d}$$

where n_a is the number of radiation-induced charge carriers available for trapping and is proportional to the dose to the phosphor (retrapping is assumed to be negligible under the Randall-Wilkins theory) and β is the trapping efficiency (the probability per unit time of a charge carrier being trapped) so that βn_a is the rate at which the traps are

filled. This equation then expresses the rate of change in the number of trapped charge carriers as affected by the accumulation of signal due to irradiation as well as the loss of signal due to their escape as indicated by the Randall-Wilkins theory. If neither β nor λ are functions of t , assumptions generally made by investigators thus employing the Randall-Wilkins theory, then the general solution of this equation for a given T is

$$n = \beta n_a / \lambda + c e^{-\lambda t}$$

If at $t=0$, $n=n_0$, where n_0 is an initial accumulation of trapped charge carriers in the dosimeter, then

$$n = \beta n_a / \lambda + (n_0 - \beta n_a / \lambda) e^{-\lambda t} \quad \text{II-e}$$

This equation (II-e) expresses the basic Randall-Wilkins theory in a form that can be directly related to the problems and situations encountered in practical dosimetry as well as a form that can be readily used to investigate the parameters of theoretical interest.

III. GENERAL RESEARCH OBJECTIVES

The general objective of this research is to critically examine the applicability of the Randall-Wilkins theory, as expressed in equation II-e, to the description of the behavior of TLD's especially under conditions typical of those encountered in common applications of thermoluminescence dosimetry, particularly those for which the ultimate purpose is the assessment of radiation dose to humans.

For most applications, including personnel, environmental, and clinical dosimetry, the use of a TLD involves the following general procedures:

(a) preparation for use - This process usually consists of cleaning, annealing (either in an oven or a reader to erase any previous signal and to re-establish sensitivity), and packaging.

(b) irradiation and/or storage - Storage may take place prior to irradiation and/or after irradiation, and is a time interval during which the dosimeter is not being deliberately irradiated. (It should be noted that irradiation at low levels is continuous due to natural environmental radiation, but this can usually be corrected for by the appropriate use of controls if it is irrelevant to the quantity of interest.)

(c) preparation for readout - This process usually consists of unpackaging, cleaning and possibly pre-readout annealing.

(d) readout - The deliberate controlled thermal stimulation of a dosimeter and the accompanying measurement of the light emitted.

Generally, (a), (c) and (d) are, or can be, performed in a reproducible manner with respect to procedures and timing. The variable

element is item (b), irradiation and storage. The following basic Regimes, illustrated in Figure III-a, indicate the situations most commonly encountered in the major applications of thermoluminescence dosimetry.

Regime I. Irradiation occurs at a typical laboratory room temperature (20°C) immediately after the preparation for use, and a period of storage, usually much longer than the period of irradiation, follows. Based on equation II-e, assuming that $n = 0$ immediately after preparation for irradiation and that during the storage interval T is constant and $n_a = 0$, the number of trapped charge carriers available to contribute to the TL response is

$$n = \left[\beta_R n_a / \lambda_R \right] \left[1 - e^{-\lambda_R (\Delta t)_R} \right] e^{-\lambda_s (\Delta t)_s}$$

where the subscripts R and s refer to the irradiation and storage intervals, respectively. Since irradiation occurs at room temperature for which the value of λ_R is expected to be very small ($< 10^{-5} \text{ sec}^{-1}$) and during a relatively short interval,

$$\left[1 - e^{-\lambda_R (\Delta t)_R} \right] / \lambda_R$$

approaches $(\Delta t)_R$ and the equation becomes

$$n = \left[\beta_R n_a (\Delta t)_R \right] e^{-\lambda_s (\Delta t)_s} \quad \text{III-a}$$

Regime II. TLD preparation is followed by a period of storage after which irradiation occurs at $\sim 20^\circ\text{C}$ immediately before preparation for readout, the irradiation period usually being much shorter than the storage period. Based on equation II-e, assuming that $n = 0$ immediately after TLD preparation and that during the storage interval T is constant and $n_a = 0$, the number of trapped charge carriers available to contribute to the TL response is

$$n = \left[\beta_R n_a / \lambda_R \right] \left[1 - e^{-\lambda_R (\Delta t)_R} \right]$$

As in Regime I,

$$\left[1 - e^{-\lambda_R (\Delta t)_R} \right] / \lambda_R$$

approaches $(\Delta t)_R$ so that this equation becomes

$$n = \beta_R n_a (\Delta t)_R \quad \text{III-b}$$

provided that β_R is not dependent on the thermal history subsequent to TLD preparation as has been generally assumed.

Regime III. Irradiation is continuous and relatively constant from the time of completion of preparation for use until the beginning of preparation for readout. Based on equation II-e, assuming that T and β are constant during irradiation and thermal history subsequent to TLD preparation, the number of trapped charge carriers available to contribute to the TL response is

$$n = (\beta_R n_a / \lambda_R) \left[1 - e^{-\lambda_R (\Delta t)_R} \right] \quad \text{III-c}$$

Regime IV. TLD preparation is followed by a period of storage, irradiation then occurs at $\sim 20^\circ\text{C}$ and a second period of storage follows before preparation for readout, the irradiation period usually being much shorter than the storage periods. This Regime is a simple combination of Regimes I and II so that the number of trapped charge carriers available to contribute to the TL response is given by equations III-a and III-b as

$$n = \beta_R n_a (\Delta t) e^{-\lambda_s (\Delta t)_s} \quad \text{III-d}$$

provided that β_R is not dependent on the thermal history subsequent to TLD preparation and where s refers only to the storage period following irradiation as in Regime I.

The difficulty with equations III-a, b, c and d, derived from the Randall-Wilkins theory, is that they only account for effects of temperature on the stability of the stored signal, i.e., already trapped charge carriers. β is assumed to be independent of temperature so that in no way do these equations allow for any effects of temperature during irradiation, or thermal history between TLD preparation and irradiation, on the ability of the phosphor to accumulate the signal.

While a wealth of experimental evidence has been accumulated in the literature (Burke, 1977), the data gathered reveal a rather chaotic situation. A considerable amount of work has been done to determine the effects of dosimeter storage on TL response for various times and temperatures following irradiation (Regime I). However, very little has been done to examine the effects on TL response of storage prior to irradiation (Regime II) or for storage both preceeding and following irradiation (Regime IV). Even less work has been done (most likely because of the experimental complexities and the length of irradiation

time required) to determine the effects of TL response of the temperature during the irradiation period itself as well as its duration (Regime III). Yet Regimes II, III and IV are encountered as frequently as Regime I for many applications of thermoluminescence dosimetry. For example, Regime III generally applies when TLD's are used for environmental monitoring and an analysis of error propagation appropriate for TLD measurements of environmental radiation has shown that errors due to time-temperature dependence are among the most significant (Burke and Gesell, 1976).

It is instructive to look at the evidence in the case of LiF, one of the most studied TLD materials. For LiF there is some support for the Randall-Wilkins theory at temperatures approaching the glow curve maximum. However, other experiments conducted closer to room temperature have produced results that are inconsistent with the theory. For example, Tobias (1972); Sunta et al., (1976); and Aitken et al., (1974) each found increases in response of about 8%, 20% and 13%, respectively, for LiF dosimeters irradiated for periods on the order of minutes at temperatures above room temperature (up to about 100°C) relative to that obtained for dosimeters irradiated at room temperature. On the other hand, Jarrett (1971) saw 15 to 30% decreases, depending on the irradiation time, in the response of LiF irradiated at either -196°C or -40°C relative to the response of dosimeters irradiated at room temperature, again a result inconsistent with the theory that predicts an increase in the loss of stored signal with increasing temperature. Further, Booth et al. (1971) obtained results showing that

the response of LiF increases by 15 and 50% after 100 and 700 hours of storage time, respectively, at 22°C prior to irradiation, an effect not accounted for at all by the theory.

In experiments designed to investigate Regime II, as well as Regimes I and IV, at room temperature, de Planque et al. (1980) also uncovered similar discrepancies with the Randall-Wilkins theory for LiF. Julius and de Planque (1983) further found for a storage temperature of 50°C prior to irradiation, decreases in TL response comparable to the decreases observed when irradiation preceded storage (up to 40%).

Unfortunately, the available data, not just for LiF, but for all commonly used phosphors, are inadequate to completely prove or disprove the Randall-Wilkins theory or to clearly support any specific theoretical modifications or alternatives. In general, interpretation of the available data is rendered difficult by experimental limitations such as very brief exposure periods and also differences among investigators in pre-irradiation or pre-storage annealing, pre-readout annealing, readout protocol, etc. All of these elements may affect the results, making any direct comparison of data from various investigators problematic at best. But perhaps the key factor limiting interpretation is that no one investigator has examined all four Regimes for which equations III-a through III-d should apply if the Randall-Wilkins theory is valid. Controlled experiments of all four types are necessary so that any other factors, e.g., annealing and readout protocol, that may affect the results can be kept constant and so that the cause of deviations from the Randall-Wilkins theory, which should be reflected differently according to the Regime, might be isolated and identified.

More specifically then, the objective of this research is to conduct experiments according to the protocol described by Regimes I through IV in order to investigate in a controlled and comprehensive manner the applicability of the Randall-Wilkins theory for describing the behavior of TLD's especially under conditions encountered in the common practice of thermoluminescence dosimetry. While, as indicted above, LiF has received considerable attention in this regard, being among if not the most commonly used phosphor, the complexity of the glow curve (obviously several levels of traps) makes interpretation for theoretical purposes extremely difficult. A more promising phosphor for interpretive purposes is $\text{CaF}_2:\text{Mn}$ which appears to have a single dosimetry glow peak. Although it is also one of the most commonly used phosphors, as well as one of the earliest (Ginther and Kirk, 1956), it has received much less attention in terms of stability, as will be shown in the next chapter, than has LiF. Therefore, in addition to providing data for the evaluation of TL theory, this research will also provide heretofore unavailable data on the behavior of $\text{CaF}_2:\text{Mn}$ in practical dosimetry situations.

The experimental plan for achieving these objectives is outlined in Chapter VI.

Fig. III-a Illustration of Regimes I (storage after irradiation), II (storage before irradiation), III (continuous simultaneous irradiation and storage) and IV (storage both before and after irradiation).

IV. CaF₂:Mn LITERATURE REVIEW

A. Brief History of CaF₂:Mn TLD's

Early development work with CaF₂:Mn powder was centered at the U.S. Naval Research Laboratory with the goal being to develop a phosphor capable of satisfying Health Physics dosimetry requirements (Ginther and Kirk, 1956). Encouraged by reasonable results, the investigators at NRL went on to design a solid dosimeter consisting of CaF₂:Mn powder imbedded in glass enamel and bonded to a copper disk. Schulman et al. (1960a) reported that this dosimeter exhibited a single glow curve peak at approximately 240° C, corresponding to a trap depth of ~1 eV and was capable of detecting 50 mR with a linear response up to at least 500 mR. Some difficulties connected with energy response and tribothermoluminescence (non-radiation induced TL, usually caused by mechanical stress) led to the development of a glass-encapsulated, or "bulb" dosimeter, the phosphor being bonded to a metal support plate with external leads which enabled heating by means of passing a constant current (about 10-15 amps for about 45 sec) through it (Schulman et al., 1960b). According to the authors, this dosimeter had a linear response from a few mR to at least 10⁵ R, was essentially independent of energy between 40 keV and 1.2 MeV, had reasonable storage properties and exhibited no tribothermoluminescence.

This, and additional work at NRL led to the development of a prototype (Palmer et al., 1966) for a system eventually manufactured commercially by Edgerton, Germeshausen and Grier, Inc. (EG+G). The system included an early model (EG+G TL-32) glass-encapsulated dosimeter with an energy compensating metal shield and an accompanying reader employing the constant current (usually ~6 amps for 10-15 sec) method. The system underwent some modifications over the years and was finally transferred in the 1970's from EG+G to Victoreen, Inc., who made additional modifications, especially to the reader. These systems, along with an essentially similar $\text{CaF}_2:\text{Mn}$ bulb system manufactured by the Harshaw Chemical Co., as well as un-encapsulated $\text{CaF}_2:\text{Mn}$ "chips" produced by the latter are widely used today, particularly in environmental (de Planque and Gesell, 1982) and personnel dosimetry.

B. Available Data on the Stability of $\text{CaF}_2:\text{Mn}$

In spite of the greater than 25 year history of $\text{CaF}_2:\text{Mn}$ as a dosimeter, the data available on the stability of this phosphor are at least restricted, if not minimal.

The bulk of the data in the literature refers to the condition defined as Regime I (see Chapter III), i.e., it is from experiments designed to investigate the effects of storing a dosimeter between irradiation and readout. Within this category several reports were found for experiments involving storage at various temperatures for intervals ranging from minutes to one year. Table IV-a lists the investigators and the major parameters associated with their experiments. 'NA' indicates

that the relevant information was not given in the report. From the table it can be seen that most of the investigators used either a Naval Research Laboratory prototype dosimeter or one of the subsequent commercial descendants. As a consequence most of the readers are of the constant-current variety rather than the types commonly used with non-bulb dosimeters which usually provide linear heating. The radiation exposures and exposure rates used, at least those indicated, fall well within the operational ranges of $\text{CaF}_2:\text{Mn}$ (Schulman et al., 1960b). In only one case (Gwiazdowski et al., 1974) was a pre-readout anneal specified. However, since a pre-readout anneal is rarely used for $\text{CaF}_2:\text{Mn}$ it is probably safe to assume that the absence of information ('NA') implies that none was used in the other cases. This may not be true for the pre-irradiation anneal (i.e., preparation for use), since some form of anneal other than the normal readout is not uncommon. It is unfortunate that this information is often missing since pre-irradiation annealing clearly may influence the outcome of stability experiments (de Planque et al., 1980, and Julius and de Planque, 1983). Of even greater impact however is the point of normalization which, by definition, affects the results. Here again, no information is provided in several cases.

The results obtained by 10 of the investigators listed in Table IV-a who examined 'room temperature' storage effects are reproduced in Figures IV-a through IV-j. Data for the remaining five who also performed room temperature tests are given in Table IV-b. The data in these figures and Table IV-b cannot be easily assimilated in this form

particularly due to the variety of methods of presentation. To eliminate this problem, all of these data have been collected into a single form in Figure IV-k. Time intervals are plotted on a logarithmic scale simply to facilitate presentation of the data extending over 7 decades. The data do not immediately appear to be consistent and it seems that no obvious conclusions may be drawn from this composite presentation.

The data available for Regime I type experiments for storage at temperatures other than room temperature are more sparse. These data have been collected in Table IV-c. The basic experimental information for these data are also given in Table IV-a. Besides the experiments of Dekker for storage intervals ranging from 1 to 15 days at 4 and 35° C, that of Schulman at 40° C for intervals up to 12 days, and the single experiment of Gwiazdowski at 40° C for an interval of 100 hours, all other experiments at temperatures other than room temperature have been performed for storage intervals of 24 hours or less, most being for intervals ranging from a few minutes to a few hours. These data, while of possible theoretical interest, leave much to be desired in terms of practical application. Comparisons are difficult at best because of the dissimilarities of storage intervals and temperatures studied.

Beyond the data for Regime I type experiments, the situation deteriorates dramatically. The only experiment following the protocol of Regime II, i.e., storage prior to irradiation, was performed by Booth et al. (1971), with an NRL-designed dosimeter. (See Table IV-a for the

basic information.) They presented data exhibiting pre-irradiation room-temperature storage effects for LiF but reported that "No corresponding change in glow curve shape or peak height with pre-exposure storage time after the last readout was observed with the $\text{CaF}_2:\text{Mn}$ dosimeters, except for a 5% loss in sensitivity after dark storage for 3 years at room temperature." However no details concerning the experiment were presented.

Four reports were found on experiments conducted according to the protocol of Regime III, i.e., continuous and simultaneous irradiation and storage. Aitken et al. (1974) reported that $\text{CaF}_2:\text{Mn}$ dosimeters irradiated at 100° C yielded a response different from dosimeters similarly irradiated at 25° C by less than 0.5%. Unfortunately, the storage/irradiation interval was not specified and no other experimental information was given. Burke (1972) performed a Regime III type experiment at room temperature using EG+G TL 32 bulb dosimeters to determine the effects of room-temperature storage during which irradiation occurred continuously for intervals ranging from 1 to 30 days. Dosimeters were prepared using only a readout; no pre-readout anneal was employed; and, readout was accomplished using constant current heating at ~6 amps for 12 seconds. The irradiation consisted of a constant cosmic ray irradiation (the dosimeters were stored in a lead shield) of $1.5 \mu\text{R h}^{-1}$ but included a much larger component of self-irradiation, about $10 \mu\text{R h}^{-1}$, due to radioactivity in the glass encapsulation. The latter component was not uniform among the dosimeters, complicating the experiment and preventing the isolation of the fading component except through

analytical methods. The analysis used assumed the validity of the Randall-Wilkins theory and produced estimates of signal loss of about 5% in one month. Later experiments by Burke (1974) followed the same protocol for storage temperatures of 52, 66, 93, 107, and 121°C. The results clearly did not support the Randall-Wilkins theory when a single trap depth and frequency factor were assumed, but rather suggested the existence of some additional time-and/or temperature-dependent phenomenon. In the absence of complementary data for experiments following the protocols of Regimes I and II, further interpretation was impossible.

Gorbics et al. (1967), see Table IV-a, had also performed an experiment following the protocol of Regime III using NRL powder in bulbs. The dosimeters were annealed at 400° C for 15 minutes prior to the experiment during which they were placed in a temperature-controlled chamber, allowed to reach equilibrium and then irradiated for seven minutes at a rate of 1 R min⁻¹ with ⁶⁰Co. Tests were conducted for temperatures ranging from -50° C to 250° C. After the seven minute irradiation, they were "promptly" removed from the chamber, returned to room temperature, and their glow curves subsequently obtained. No effects were seen up to 175°C but the loss of signal increased above that to about 25% at close to 250° C, all relative to the results obtained for the seven minutes irradiation at 25° C. As discussed by the authors, the storage/irradiation interval was short relative to the times needed to establish temperature equilibrium both before and after the irradiation/storage interval. This aspect of the experiment essentially prohibits any quantitative analysis

of the results, although the authors suggested that the results, very qualitatively, appeared to be not inconsistent with their Regime I experiments conducted at similar temperatures for twenty minute storage intervals (Table IV-b).

No $\text{CaF}_2\text{:Mn}$ experiments were found following the protocol of Regime IV.

In summary, while a fair number of investigations have been made of the stability of $\text{CaF}_2\text{:Mn}$, most of these have been pure fading, i.e., Regime I, experiments. These data appear to be too scattered to suggest any interpretation. The one Regime II experiment and the four Regime III experiments likewise provide no solid conclusions. The data available undoubtedly leave some uncertainty concerning the performance of $\text{CaF}_2\text{:Mn}$ in practical applications and surely, there is no clear-cut evidence to support any firm theoretical considerations regarding the behavior of this phosphor.

TABLE IV-a
DATA AVAILABLE ON THE STABILITY OF $\text{CaF}_2:\text{Mn}$ (Regime I)

AUTHOR	PHOSPHOR TYPE	IRRADIATION			READOUT PROTOCOL	ANNEALING		NORMALIZATION	RESULTS	LEGEND
		SOURCE	EXPOSURE	RATE		PRE IRRADIATION	PRE-READ			
Becker et al. (1971)	Harshaw powder	NA	NA	NA	linear ramp	NA	NA	NA	TABLE IV c	
Booth et al. (1971)	NRL glass needle	^{60}Co	12.5 R	2.5 R min^{-1}	constant current for 17 sec	None	None	10 min after irradiation	Fig. a	▽
Dekker (1976)	EG+G TL-32 bulb	^{137}Cs	5-50 mR	NA	constant current	unspecified anneal	NA	NA	Fig. b TABLE IV c	+
Fitzsimmons and Horn (1972)	EG+G TL-32 bulb	probably ^{137}Cs	400 mR	NA	constant current	unspecified	NA	NA	Fig. c	▼
Gayton et al. (1972)*	NA	NA	NA	NA	NA	NA	NA	NA	TABLE IV b	⊕
Gorbics et al. (1967)	EG+G TL-32 bulb	^{60}Co	4 R	NA	constant current $\sim 25^\circ\text{C sec}^{-1}$	400° 30 min	NA	~6 min. after irradiation midpoint	Fig. d	■
Gorbics et al. (1967)	NRL powder in bulb	^{60}Co	10 R	1 R min^{-1}	constant current	400° 15 min	NA	20 min. after irradiation	TABLE IV c	
Gross (1976)	Victoreen 2690-46 (=EG+G TL-32 bulb)	^{226}Ra	probably 5-12 mR	NA	constant current	NA	NA	24 h after irradiation	Fig. e	□
Gwiazdowski et al. (1974)	homemade powder	^{226}Ra	50 mR- 13.4 R	NA	NA	1.5 h at 400° 7 min at 100°, cool 2 h at 100°C	1 day, room temp. 5 min at 110°C	NA	TABLE IV c	

TABLE IV-a (Cont'd)

AUTHOR	PHOSPHOR TYPE	IRRADIATION			READOUT PROTOCOL	ANNEALING			RESULTS	LEGEND
		SOURCE	EXPOSURE	RATE		PRE IRRADIATION	PRE-READ	NORMALIZATION		
Johnson and Attix (1967)	NRL (EG+G manufactured) prototype bulb	NA	4 R	NA	constant current	NA	NA	6 min after irradiation	Fig. f	△
Kiefer et al. (1969)*	NA	NA	NA	NA	NA	NA	NA	NA	TABLE IV b	⊗
Palmer et al. (1966)	NRL (EG+G manufactured) prototype bulb	NA	NA	NA	constant current for 12 sec	NA	NA	NA	TABLE IV b	#
Partridge et al. (1973)	EG+G TL-15 bulbs	²²⁶ Ra or ¹³⁷ Cs	1m R-5 R unspecified	NA	constant current	unspecified anneal	NA	'no time delay between exposure and readout	TABLE IV b TABLE IV c	#
Schulman et al. (1960)	NRL bulb	probably ⁶⁰ Co	200 mR and 10 10 R	NA	constant current for 45 sec	NA	NA	NA	Fig. g TABLE IV c	○
Schulman et al. (1969)	EG+G TL-32 bulb	NA	4 R	1R min ⁻¹	constant current for ~12 sec ~25° sec ⁻¹	NA	NA	2 min after irradiation	Fig. h TABLE IV c	●
Spurny and Kvasnicka (1974)	commercial, unspecified	NA	50-100 R	'short'	NA	unspecified anneal	NA	.1 h, inferred from Fig. i	Fig. i	▲
Uran (1971)	homemade discs	probably ⁶⁰ Co	NA	NA	linear ramp, probably between 3 and 30° sec ⁻¹	NA	NA	<15 min, inferred from Fig. j	Fig. j	X
Wintle et al. (1971)	powder	β source	100 rads	NA	6° C sec ⁻¹	NA	NA	'readout immediately after irradiation'	TABLE IV b TABLE IV c	⊗

NA - Not Available

* Work apparently not done by author, but no reference is given.

Table IV-b

Data for Regime I Type Experiments Conducted at Room Temperature

Author	Storage Interval (hours)	Remaining Signal
Gayton et al. (1972)	758	0.90
Kiefer et al. (1969)	24	0.94
	758	0.90
Palmer et al. (1966)	1,516	1.00
Partridge et al. (1973)	24	0.96
Wintle et al. (1971)	18	0.94 - 0.96

Table IV-c

Data For Regime I Type Experiments Conducted at Temperatures
Other than Room Temperature

Author	Temperature (°C)	Storage Interval (hours)	Remaining Signal
Gorbics et al. (1967)	-25	0.3 ^a	1.00
Wintle et al. (1971)	-18	18	0.94 - 0.96
Partridge et al. (1973)	- 8	24	0.97
Dekker (1976)	4 ^d	0 ^a	1.00
		24	0.95
		72	0.94
		144	0.94
		240	0.90
		360	0.92
	35	0 ^a	1.00
		24	0.91
		72	0.91
		144	0.92
		240	0.93
		360	0.90
Schulman et al. (1960)	40	0-289	same as for 25°C (see Fig. IV-g)
Gwiazdowski et al. (1974)	40	100	0.92
Partridge et al. (1973)	54	24	0.95
Wintle et al. (1971)	65	18	0.93
Uran (1971)	65	0.5	0.99
		1.0	0.98
		1.5	0.98
		2.5	0.98
		4	0.98
		5	0.98
		6	0.98

Table IV-c (cont'd)

Author	Temperature (°C)	Storage Interval (hours)	Remaining Signal
Gorbics et al. (1967)	100	0.3 ^b 0-4	1.00 down to 0.95 (see Fig. IV-d)
Becker (1971)	100	504	0.80
Gorbics et al. (1967)	125 150	0.3 ^b 0.3 ^b 0-4	1.00 0.99 down to 0.84 (see Fig. IV-d)
	175	0.3 ^b 0-2	0.96 down to 0.70 (see Fig. IV-d)
	194	0.3 ^b	0.91
Schulman et al. (1969)	200	1	0.99 ^c
Gorbics et al. (1967)	200	0-0.5	down to 0.74 (see Fig. IV-d)
	220	0.3 ^b	0.76
	248	0.3 ^b	0.42
Schulman et al. (1969)	250	1	0.30 ^c
	270	1	0.12 ^c
Gwiazdowski et al. (1974)	environmental ^e	2280	0.70-0.72

^a Actual normalization interval, quoted as '0', not specified.

^b Normalized to reading for dosimeter stored for .3 h at 25° C after irradiation.

^c Inferred from glow curves.

^d Text says data are for '4° C', Table in text lists '40° C'; however position in the table supports 4°.

^e Experiments conducted out-of-doors, temperature profiles not indicated in paper.

Fig. IV-a Variation of glow-peak height as a function of storage time in darkness at 22°C. Points represent averages of 10 dosimeters. (After Booth et al., 1971).

FIG. IV-b Variation of the TL signal from a single dosimeter as a function of storage time at 24°C. (After Dekker, 1976).

FIG. IV-c Variation of glow-peak height as a function of storage time at room temperature. The data points are mean values with $\pm$ one sigma shown by vertical lines. (After Fitzsimmons and Horn, 1972).

FIG. IV-d Variation of glow-peak height as a function of storage time at various temperatures. Points represent averages of 3 dosimeters. (After Gorbics et al., 1967).

FIG. IV-e Ratio for storage time t at room temperature derived by dividing the glow-peak height for $t = 24$ hours by the glow-peak height for t , (i.e., data are expressed as a correction factor for dosimeters stored for periods other than 24 hours). Each data point obtained consisted of the mean of four measurements. (After Gross et al., 1976).

FIG. IV-f Variation of glow-peak height as a function of storage time at 24°C. (After Johnson et al., 1967.)

FIG. IV-8 Variation of glow-peak height as a function of storage time in the dark at room temperature. (After Schulman et al., 1960b).

FIG. IV-h Variation of glow-peak height as a function of storage time in the dark at 24° C. (After Schulman et al., 1969).

FIG. IV-i Variation of glow-peak area as a function of storage time at room temperature. Each point represents the mean of 10 readouts of each of 10 dosimeters. The curve was obtained from a computer calculation using the least square method to fit a curve up to a polynomial of degree 5. (After Spurny and Kvasnička, 1974).

FIG. IV-j Variation of glow-peak height as a function of storage time at 20°C. (After Uran et al., 1971).

FIG. IV-k Variation of the TL signal as a function of storage time at 'room temperature'. Data taken from Figures IV-a through IV-j and Table IV-b. See Table IV-a for the legend.

V. EXPERIMENTAL PLAN AND EQUIPMENT

A. Experimental Plan

In order to obtain more information concerning both the theoretical and practical questions left unanswered by the data already available in the literature, a basic plan was established to conduct experiments according to the protocol described in Chapter III for Regimes I, II, III and IV. It was decided that both practical and theoretical interests would be served by investigating storage/irradiation intervals ranging from about one day to one week for temperatures of -25 , $+20$, $+65$, $+150$ and $+175$ degrees celsius. Tests at 20°C were deemed essential both for direct comparison of results with the available ''room temperature'' data and because room temperature effects are encountered in virtually every practical situation due to the usual laboratory preparation, possible irradiation, and/or storage, and eventual readout of dosimeters. A lower temperature was considered to be of theoretical importance especially because of the almost complete absence of data below room temperature and because two of the three results (Table IV-c) found in the literature suggested fading of a magnitude greater than that found at room temperature, a result obviously contrary to the Randall-Wilkins theory. A temperature of -25°C was chosen for this purpose because the existing data suggest that this is sufficiently lower than room temperature to permit the observation of effects and because it represents a reasonable lower limit for practical applications, specifically, environmental monitoring. This application also suggested $+65^{\circ}\text{C}$ as a reasonable upper limit for practical consideration. While 65°C is not a commonly

encountered ambient temperature, it has been shown by Gesell et al. (1980) that, because of protective packaging, dosimeters in the environment are frequently exposed to temperatures at least 15°C above ambient principally due to solar radiation. It is probable that effects at ~36°C, a temperature of particular interest for in vivo medical dosimetry could be conservatively estimated from effects observed at +20 and +65°C. In anticipation of possible relatively small effects in the -25 to +65°C range, the two high temperatures, +150 and +175°C were chosen to facilitate the analysis of results for theoretical purposes. The details of the protocol and time schedules were determined following preliminary dosimeter testing and are given in Chapter VI.

B. Equipment

The basic equipment used to carry out the experimental plan included the $\text{CaF}_2:\text{Mn}$ dosimeters, special dosimeter packaging, a TLD reader with an associated Hewlett Packard 85 mini-computer for data storage and glow curve analysis, an annealing oven and annealing tray for dosimeter preparation, an environmental test chamber, a ^{137}Cs irradiation facility and a lead shield for control experiments.

1. $\text{CaF}_2:\text{Mn}$ dosimeters - The form of $\text{CaF}_2:\text{Mn}$ chosen is the solid, or "chip" dosimeter manufactured by the Harshaw Chemical Company.* For this experiment it was considered preferable to the bulb, or glass-encapsulated chip, dosimeter

* The Harshaw Chemical Company
Crystal and Electronic Products Department
6801 Cochran Road
Solon, Ohio 44139

of the types made by the Naval Research Laboratory and later manufactured by EG+G, Victoreen and Harshaw, primarily because of lack of ambiguity associated with the direct exposure of the phosphor to the environmental test conditions. The phosphor is prepared using the standard coprecipitation technique (Palmer et al., 1965). The basic properties are given in Table V-a.

2. Dosimeter Packaging - Two basic types of dosimeter packages were used. Figure V-a shows the package designed to hold the $\text{CaF}_2:\text{Mn}$ chips during testing in the environmental chamber. The holder is made of Teflon, chosen because it would not interact with the phosphor (as might several metals, mainly through oxidation) and because it would maintain its physical integrity over the required experimental time and temperature ranges. It is designed in two pieces, a bottom piece with holes cut to provide recesses for up to 15 chips, and a matching top piece to hold the chips in place. The entire package allows the direct exposure of almost the entire surface area of the chip to the ambient atmosphere. Figure V-b shows the packages used during irradiation at the ^{137}Cs calibration facility. The basic container is a commercially-available plastic box with hinges and a snap closure. These boxes have been fitted with various lucite inserts providing recesses for holding chips in either 5 by 5 or 4 by 4 matrices (as shown in Figure V-b) or in up to 10 recesses for individual chips. These boxes have been tested with both LiF and $\text{CaF}_2:\text{Mn}$ chip

dosimeters at the ^{137}Cs calibration facility to ensure that all chips are irradiated uniformly. All types of packaging and handling procedures used in the experiment permitted retention of the identity of the unmarked individual chips by means of placement.

3. TLD Reader - The TLD reader used was designed and built at the Environmental Measurements Laboratory (EML) as a research reader and is one of the two virtually identical readers used in the laboratory's TLD programs for over a decade. Shown in Figure V-c, it has multiple components with almost all front panel adjustments and selectors to provide the ease of flexibility required in research programs. The unit on the left houses the high gain, low noise photomultiplier tube (EMI 6256 SA) cooled electronically to -15°C below ambient temperature and a drawer assembly directly beneath it containing a heater pan for placement of the chip during readout. The pan is made of thin silver soldered to an electronically controlled heating element. A removable platinum-plated stainless steel disc with a central recess corresponding to the size of the TLD chips rests on the heater pan providing a reproducible geometry for chip placement and suppression of unwanted infrared signal from the pan. The reader is designed to provide linear heating at a variety of heating rates up to a maximum temperature of $\sim 550^{\circ}\text{C}$ and provides the option for maintaining a constant temperature

level at any temperature up to 550°C for a variety of time intervals at the end of the linear ramp. The drawer assembly also contains a permanent light source for checking the electronic stability of the system. During operation, gas (99.998% pure nitrogen) flows through the heating chamber at a rate of 5 standard cubic feet per hour to suppress any non-radiation induced thermoluminescence signal.

The rack on the right contains all of the electronic controls including those for the PM tube high voltage, the heating system, and the signal output. The TL output is displayed in glow curve form along with the heating profile on the chart recorder shown on the top of the electronic control bins. The TL signal is also provided in digital form with front panel controls allowing for the setting of the start- and stop-integration points at any desired positions during the heating cycle. Figure V-d shows a schematic of the basic elements of the reader system.

An additional data acquisition system was designed for this experiment and is shown in Figure V-e. The Hewlett Packard 85 mini-computer was programmed to automatically accept the TL signal for each readout from the TLD reader and store it in glow curve form on magnetic tape. The figure shows a typical $\text{CaF}_2:\text{Mn}$ glow curve displayed on the CRT. A program was written to analyze the stored data in various ways including the integration of the TL signal between any selected points

on the glow curve as well as the combination of any two or more glow curves.

4. Annealing Tray - The tray used for annealing TLD chips prior to use is shown in Figure V-f along with the Teflon-tipped vacuum pen used for all dosimeter handling. (The latter minimizes mechanical insult to the chips as well as chemical contamination thereby minimizing chemoluminescence and triboluminescence.) Designed at EML, the tray consists of a copper base, treated with a flash of nickel and coated with platinum. This construction is intended to provide an optimum balance between good heat conductivity and prevention of any chemical interaction between the tray and the chips. The indentations permit retention of individual chip identity by placement.

5. Annealing Ovens - Three annealing ovens shown in Figure V-g, were used in these experiments, a Blue M Rad-O-Glow furnace, a Fisher Isotemp Oven, Junior Model, and a Blue M Lab-Heat Muffle Furnace.

All three ovens were kept at a single temperature continuously to facilitate annealing reproducibility. The first two, kept at 400 and 100°C respectively were used for annealing LiF chips used for TLD system controls. The Blue M Lab-Heat muffle oven, shown in more detail in Fig. V-h, was kept at 500°C and used for the annealing of $\text{CaF}_2\text{:Mn}$ chips.

6. Environmental Test Chamber - Figure V-i shows the environmental chamber used for these experiments. It is a Tenney* Model BTR-Benchmaster test chamber. The unit has a temperature range of -73° to $+177^{\circ}\text{C}$ with a control tolerance of 0.4°C and an inner work space 51 cm wide, 56 cm high and 50 cm deep. Figure V-j shows the inside of the chamber with a typical dosimeter configuration. In addition to the built in temperature sensor and controller, an additional temperature sensor (Stolab Model 921 PL) was installed in the chamber center (see Figure V-j) for quality control and as an emergency backup. The unit on the upper right of the main chamber, shown in Figure V-i, provided a continuous (LCD) display of the temperature measured with the built in sensor and the unit on the upper left, a Newport Digital Data Printer (Model 810) provided a printed record every ten minutes. A continuous chart record of the additional temperature sensor was provided on the Soltec (Model S-4202) Recorder shown in middle.

* Tenney Engineering, Inc.
1090 Springfield Road
Union, NJ 07083

7. ^{137}Cs Calibration Facility - All irradiations for these experiments were performed at the EML ^{137}Cs Calibration Facility, shown in close-up in Figure V-k. The lead housing, with a manual shutter, contains a collimated ~ 3 Ci ^{137}Cs source. The radiation beam produced is uniform over a diameter of 3.5 cm at 1 M and 6.0 cm at 2 M and the exposure rates were 13.9 and 3.5 mR min⁻¹, respectively, at the time the experiments were performed. The figure shows an irradiation package in place at the one meter position. The calibration is traceable to the National Bureau of Standards and the beam geometry and exposure rates are checked regularly at the 1, 2, 3, 4 and 5 meter positions (Burke et al., 1976). The uncertainty associated with irradiation reproducibility is estimated to be $< \pm 0.2\%$ for these experiments. The uncertainty in the accuracy of the exposure is less than 1%.

Table V-a

Properties of the Harshaw $\text{CaF}_2:\text{Mn}$ Chip Dosimeter ^a

Dimensions:	3.17 x 3.17 x 0.9 mm
Density:	~3.1 g cm ⁻³
Effective Atomic Number:	~16.3
TL Emission Spectrum:	4400-6000 Å, ~5000 Å maximum
Temperature of TL Glow Peak:	~300°C
TL Response Ratio, 35 keV/ ⁶⁰ Co Energy:	~15
Usable Range:	from less than 1 mR to greater than 10 ⁵ R

^a

Source: Product Bulletin, Harshaw Chemical Co.

Figure V-a. Teflon packages used to hold CaF₂:Mn chips during testing in the environmental chamber.

Figure V-b. Lucite packages used to hold TLD chips during irradiation at the ^{137}Cs calibration facility.

Figure V-c. Environmental Measurements Laboratory's TLD reader.

A. HEATER PAN

B. THERMOCOUPLE IN CONTACT WITH
HEATER PAN

C. TLD

FIG. V-d Schematic of the basic elements of a TLD Reader.

Figure V-e. Hewlett Packard 85 mini-computer used to process glow curve information from the TLD reader

Figure V-f. Annealing tray and vacuum pen used to anneal and handle TLD chips.

Figure V-g. Ovens used for annealing TLD chips.

Figure V-h. Oven used for annealing $\text{CaF}_2\text{:Mn}$ TLD chips at 500°C .

Figure V-i. Environmental Test Chamber used for TLD stability tests.

Figure V-j. Interior of the Environmental Test Chamber with $\text{CaF}_2\text{:Mn}$ chips in place in Teflon packages.

Figure V-k. ^{137}Cs calibration facility with TLDs in a lucite package in place at a distance of 1 meter from the source for irradiation.

VI. PRELIMINARY TESTING AND PROTOCOL DEVELOPMENT

A. Preliminary Testing

In practice, the general preliminary testing of a TLD system is essentially an iterative process in which various parameters are frequently adjusted in a manner determined by the experience of the investigator with the multiple components of the system. Preliminary testing of the system used for these experiments was conducted to collect basic information regarding the performance of the system, assess potential problems, identify factors possibly interfering with properties to be examined, and determine the optimal specific protocol for the experiments to be performed. Tests were conducted to determine the optimal readout parameters and anneal protocol, the uniformity and reproducibility of dosimeter response, and the linearity of response over the expected exposure range, and to investigate the existence of any self-irradiation or problems associated with the types of dosimeter packaging chosen. These tests were conducted according to the basic testing principles delineated in the applicable ANSI Standard (ANSI, 1975). $\text{CaF}_2\text{:Mn}$ chips, chosen at random from the virgin manufacturing batch set aside for these experiments, were used for the preliminary testing.

1. Preparatory Anneal and Readout Parameters

Both relevance to common dosimetric practice and theoretical interests had to be balanced in the choice of the readout and annealing protocols. An examination of Table IV-a reveals that a variety of

different preparatory anneals have been employed in practice for $\text{CaF}_2:\text{Mn}$ ranging from none to the order of minutes to hours at 400°C . In addition, however, Lucas and Kapsar (1974) have shown that for doses exceeding 1000 R, a high temperature (well over 500°C) trap is activated in $\text{CaF}_2:\text{Mn}$ which eventually can cause a build-up, or residual signal, in the normal dosimetric trap. They showed that this effect can be eliminated by using a preparatory anneal of 500°C for 1 hour. Taking all this into account, several anneals involving 15 minutes to one hour at both 400 and 500°C were tried in conjunction with a variety of readout parameters. Since all previous investigators except one (Table IV-a) have not used a pre-read anneal, and since there appears to be no evidence (no significant peak $< \sim 150^\circ\text{C}$) warranting a pre-read anneal, none was used for these experiments. Again referring to Table IV-a, the overwhelming majority of investigators have used the "constant current" readout technique. This of course is the standard technique used for bulb dosimeters and involves passing a current of about 6 amps through the bulb dosimeter wiring to heat the phosphor for a period of several seconds (usually 10-20 seconds and almost always under one minute). This technique, however, does not allow an adequate determination of the heating profile of the dosimeter. Therefore, the use of a linear (constant rate) heating is much more desirable from a theoretical point of view for identifying the temperature of glow peaks and permitting the use of various forms of the Randall-Wilkins formula containing the heating rate as a factor. Considering the desire for both practical and theoretical application, it was therefore decided to employ a linear

heating ramp using a rate that would accomplish readout in the commonly used time intervals of several seconds to less than one minute. It was also decided to measure the integrated readout signal with the peak option also available. Several hundred readouts were then performed to determine the effects of the various preparatory anneals and to select the optimal readout parameters. For a given readout protocol, increases in both the signal (first readout of an irradiated dosimeter) and the background (second readout of an irradiated chip or first readout of an unirradiated chip), as well as decreases in the signal-to-noise (background) ratio, were observed as either the annealing time or temperature increased. In spite of the decreased signal-to-noise ratio and in order to avoid any possible complications associated with the high temperature trap (Lucas and Kapsar, 1974) it was deemed best to choose a preparatory anneal of 1 hour at 500°C in anticipation that the exposure levels involved would be high enough to avoid any difficulties associated with the slightly decreased signal-to-noise ratio. Reader parameters, mainly the heating rate, the maximum temperature, and the start- and stop-integration points were adjusted in order to maximize the signal-to-noise ratio, minimize the infrared signal, and provide reasonable glow curve resolution within the already selected heating rate constraint. The settings finally chosen provided a 17 second readout cycle using a linear temperature ramp with a heating rate (pan temperature) of approximately 25°C per second. Figure VI-a shows a typical glow curve processed through the HP 85 minicomputer for a single chip given an irradiation of 97 mR, and Figure VI-b shows an analagous composite (average) glow curve

for 145 chips. Signal integration was performed between channels 217 and 445. (Detailed analysis of the glow curve is given in Chapter VII.) These annealing and readout protocols were used throughout the remaining preliminary testing and experiments.

2. Uniformity and Reproducibility of Dosimeter Response

One hundred and fifty virgin chips, arbitrarily numbered 1000 through 1149, were selected at random from the batch to test the uniformity and reproducibility of dosimeter response. In preliminary tests on six separate occasions all 150 chips were annealed, then irradiated in groups of 25 (in the irradiation packages shown in Figure V-b) at a distance of 1 meter from the source at the ^{137}Cs calibration facility. The exposures were $97.6 \pm 0.2\text{mR}$ (precision uncertainty). Readouts were then performed using an interspersed technique, i.e., chips numbered 0, 5, 10, ... 145 were read in sequence followed by chips numbered 1, 6, 11, ... 146 in sequence etc. This technique is used to minimize the effects of any systematic variation in instrument parameters (such as reader sensitivity) during the readout. All chips, as usual throughout these experiments, were read twice in succession, with the second readout regarded as the chip background and the net signal attributed to the irradiation. The results are shown in Table VI-a for 30 groups of five chips. Across the bottom of the Table are given the net integrated counts averaged over the means of the thirty groups, the absolute and percent standard deviations of a single group mean from the overall mean and the ratio of the mean of the highest group of five to the lowest group of five. The body of the table contains the ratios of

the mean of each group of five to the overall mean. The columns at the right indicate the means and standard deviations of these ratios for each group of five chips over the six uniformity tests. These test data show that the reproducibility of the relative responses of the 30 groups is clearly better than the uniformity of response among the thirty groups, indicating that corrections for differences in relative sensitivity should improve all experimental data. Analogous data from these tests are shown for 15 groups of 10 chips each in Table VI-b with the expected similar results regarding uniformity and the reproducibility of relative response. (The steady decline in the overall means with time has no effect on these conclusions and will be discussed further in Chapter VII.) These results are summarized in Table VI-c. In addition, this table shows the effect of using the relative sensitivity ratios obtained from any one test to correct the results of the subsequent test for the thirty groups of 5 chips. The standard deviations and maximum-to-minimum group ratios for the results so corrected are given in the last two columns of the table. These data for the preliminary uniformity tests indicate that by using groups of five chips, corrected for differences in relative response, one can expect a measurement precision of about 1% (1 standard deviation)*. This expectation is further supported by the results obtained from additional uniformity tests repeated throughout the experiments for quality control and given at the bottom of Table VI-c.

* These 150 chips were set aside for use in the actual stability experiments.

3. Linearity

Another one hundred fifty virgin chips chosen at random from the batch were tested for uniformity of response as just described and relative sensitivity correction factors were calculated for the fifteen groups of 10 chips. They were then annealed and irradiated in groups of ten with exposures ranging from 0 mR (no irradiation) to 175 mR. Irradiations were performed at either one or two meters from the ^{137}Cs source and irradiation times ranged from 1.2 minutes in the case of the lowest actual irradiation up to 12.1 minutes in the case of the highest. Uncertainty (precision) in the exposure determination was estimated to be less than 1%. The chips were read out, again using the interspersed technique, reading one chip from each exposure group, then a second from each group, etc. The results are shown in Figure VI-c. The response is linear with a correlation coefficient of 0.9988.

4. Self-irradiation and Packaging Effects

One hundred fifty virgin chips were chosen at random from the batch to test for self-irradiation and to examine any effects introduced by the types of packaging used. The chips were used in groups of 10 rather than employing groups of 5 with sensitivity correction factors to avoid masking any possible compensating effects. Four types of packaging were used in this test: the Teflon holder designed for use in the environmental test chamber (Fig. V-a), the plastic holder used mainly for irradiation (Fig. V-b), the Teflon holder sealed in an air-tight zip lock plastic bag, and the conventional metal capsule used to hold the EG+G/Victoreen commercial bulb dosimeters.* The plastic-sealed Teflon package was used

to test for any effects related to the direct exposure of the chips to the environment, and hence to a whole host of possible unknown environmental contaminants, that would occur when the Teflon holders would be used alone. The metal capsules were tested mainly to identify any energy response difficulties. Energy response problems could be expected to be enhanced in the absence of the standard metal capsule, basically designed to compensate for the enhanced response of CaF_2 at low energies. No difference in results between the metal-encapsulated chips and the other chips could be taken as an indication of the absence of any significant soft (<100 keV) component in the spectra in the locations where the chips were placed for testing. Three locations were investigated in this test: the environmental test chamber, the TLD Reader Room, and the lead shield used for dosimeter storage and as a quality control test location throughout the experiments. For this test 110 chips were initially annealed, and forty were reserved to be used as calibration controls. The annealed chips were immediately placed, un-irradiated, in the various test packages and then stored in the test locations for one month. Just before readout the remaining forty chips were annealed and given appropriate calibration irradiations. All chips were

* Ten chips were held in identifiable positions within each metal capsule by primary packaging in a cut-off plastic drinking straw with a diameter just exceeding the diagonal of the chip.

then read out using the interspersed technique. The results are shown in Table VI-d. Within each location there are no significant differences or trends as a function of packaging type, suggesting no obvious problems due to energy response or environmental insult. The data do indicate, however, a self-irradiation effect. The exposure rate in the lead shield is well known from innumerable measurements made over the past decade to be $1.55 \mu\text{R h}^{-1}$, which indicates an excess of approximately $9.3 \mu\text{R h}^{-1}$ if the assumption is made that the phosphor is perfectly stable at room temperature, i.e., there is no fading or sensitivity change under the temperature conditions and within the 30 day period used for the test. Previous LiF measurements in the environmental test chamber yielded an exposure rate of $\sim 7 \mu\text{R h}^{-1}$ resulting in a self-irradiation of $9.4 \mu\text{R h}^{-1}$ for the $\text{CaF}_2:\text{Mn}$ chips stored in the chamber, in excellent agreement with the lead shield results. A consultation with the manufacturer revealed that indeed, a complete manufacturing batch of $\text{CaF}_2:\text{Mn}$ chips appeared to be contaminated. Fortunately however, the contamination seems to be extremely uniform. For the purpose of the experiment, rather than being a disadvantage, this feature is a bonus in that the combination of the self-irradiation rate and the natural background exposure rate in the environmental chamber provide a constant irradiation rate appropriate for tests following the protocol of Regime III.

B. Detailed Experimental Protocol

Determination of the specific protocol to be followed for the stability experiments under Regimes I through IV primarily involved

balancing several factors to achieve minimal uncertainty. Precision certainly increases with the number of chips used both for measurements and for calibration controls and also with higher irradiation levels (lower errors due to irradiation timing uncertainties). However larger numbers of chips and higher exposures increase the time involved for handling, irradiation, and readout and hence increase timing uncertainties in an experiment investigating phenomena as a function of time.

Having weighed these parameters, it was decided that 5 chips would be used for each measurement and 10 chips for each of the main calibration controls, with relative sensitivity correction factors applied in all cases. The larger number was chosen for calibration controls purely as a matter of ''safety'' or ''insurance''. Any losses in this category would result in a significant data loss or precision decrease, since it would affect all data for a particular readout whereas an equivalent loss from a group used for single measurement would only have an impact on that single measurement.

A level of ~100 mR was chosen for the irradiations required in Regimes I, II and IV. In practice, the irradiation time was fixed at 7 minutes at a distance of 1 meter from the ^{137}Cs source, and the precise exposure determined taking into account decay over the several months required to complete the testing and experiments. The exposure level, irradiation time, and distance from the source, were selected to minimize the overall uncertainty as indicated above and provide exposures within the range tested for linearity.

To ensure experimental reproducibility, a general schedule given in Table VI-e, was devised for all activities and adhered to rigidly throughout the experiments. The 150 chips used in the preliminary testing for uniformity and reproducibility of relative response were chosen for the stability experiments and assigned as indicated in Table VI-f.

Tests for all Regimes and time intervals of interest were conducted for a specific temperature, and then the entire process repeated at the next temperature of interest, the temperatures studied being -25, +20, +65, +150 and +175°C. Six time intervals were selected for study being nominally 1, 2, 3, 5, 6, and 7 days, and exactly 17, 41, 65, 113, 137, and 161 hours, as determined by the general schedule given in Table VI-e. To minimize the risk of variations in temperature, and to minimize the uncertainties associated with variations in annealing and readout, the schedule for experiments at any given temperature was designed to minimize the total number of days and the number of readouts required given the number of chips used. To accomplish this, the schedule for a single temperature for Regimes I, II and III involved four separate preparations and four separate readouts, with three assigned categories of dosimeters (A, B and C in Table VI-f) being used to obtain data for the six storage intervals. Table VI-g indicates how three categories, A, B, and C, of chips can each be used twice within a total interval of eight days to obtain all six storage intervals of interest. The particular combination used for any given temperature was chosen at random. Seven categories of chips were required to obtain data for Regime IV since all of these chips required a total storage time of eight days to make up all of the pre-

and post-irradiation storage interval combinations investigated under Regimes I and II. The Regime IV experiment required one preparation, and irradiation, on days 1, 2, 3, 5, 6 and 7 (one category each day) of the total eight day period, and a final readout on the eighth day.

For each of the five temperatures studied, as a form of quality control, category D chips were simultaneously used to obtain analogous Regimes I, II and III data for a storage interval of ~8 days (185 hours) in the lead storage shield kept at normal laboratory temperature in the TLD Reader Room. In addition, another group of chips (listed as background controls in Table VI-f) was used to repeatedly measure natural background for the same six 185 hour intervals just outside of the environmental test chamber, also as a quality control check.

Every readout included one set of 10 calibration control chips annealed and irradiated (~100 mR, exactly 7 minutes at 1 meter from the ^{137}Cs source) within one hour of the start of the readout (see Table VI-c) and used as the normalization point for all measurements. Additional controls were used to verify linearity with calibration exposures in the range of the exposures obtained for the Regime III chips.

Every readout session included routine quality control measurements, at both the beginning and end, of the dark current (signal obtained during a readout cycle with the heat off and no chip in place), the chamber current (signal obtained during a readout cycle with the heat on and no chip in place) and the TLD Reader built-in light source. Also, LiF chips were read out during each readout session as a check on TLD Reader stability, and as an additional quality control check on the $\text{CaF}_2\text{:Mn}$ cal-

ibration controls. One hundred fifty chips were used for this purpose. They were tested for uniformity and reproducibility of relative response in the same manner as that used for the $\text{CaF}_2\text{:Mn}$ chips. The LiF data are shown in Table VI-h. For use as Reader stability indicators they were all annealed simultaneously according to EML standard procedures (Harley, 1972), irradiated prior to the start of the $\text{CaF}_2\text{:Mn}$ experiments, and stored in the lead shield. For each $\text{CaF}_2\text{:Mn}$ readout session, 10 LiF chips were removed from the lead shield and read out along with the $\text{CaF}_2\text{:Mn}$ chips using the interspersed technique. The data were corrected for differences in relative sensitivity based on the results of the uniformity tests. A second round of annealing and irradiations were required to supply enough LiF chips for all of the $\text{CaF}_2\text{:Mn}$ readouts. A set of 10 chips from the first anneal were reserved for readout along with a set of chips from the second anneal to insure no difference attributable to anneal variations. The stability of these LiF chips, required for this purpose, was verified in experiments reported by de Planque et al (1980).

Table VI-a
Uniformity and Reproducibility of $\text{CaF}_2\text{:Mn}$ Chip Response
(5 Chips per Group)

Dosimeter Group ^a	Dosimeter Group Counts/Mean Counts						Mean	1 Std. Deviation
Test Date:	8/24/81	8/27/81	8/28/81	9/01/81	9/03/81	9/10/81		
1000	1.0011	1.0107	0.9775	1.0092	1.0079	1.0045	1.0018	0.0124
1005	1.0027	1.0242	1.0304	1.0288	1.0232	1.0202	1.0216	0.0099
1010	1.0058	1.0107	0.9980	1.0129	1.0148	1.0166	1.0098	0.0069
1015	0.9934	1.0139	1.0209	1.0269	1.0269	1.0190	1.0168	0.0125
1020	0.9960	1.0006	0.9919	0.9946	1.0031	1.0049	0.9985	0.0051
1025	1.0046	1.0241	1.0271	1.0233	1.0278	1.0203	1.0212	0.0086
1030	0.9935	0.9960	0.9932	0.9900	0.9907	1.0048	0.9947	0.0054
1035	0.9955	1.0199	1.0211	1.0257	1.0259	1.0167	1.0175	0.0113
1040	1.0132	1.0188	1.0253	1.0139	1.0154	1.0288	1.0192	0.0065
1045	0.9933	1.0051	1.0069	1.0021	1.0079	1.0012	1.0028	0.0053
1050	1.0110	0.9993	1.0066	0.9988	0.9994	1.0167	1.0053	0.0074
1055	1.0042	1.0068	1.0111	1.0051	1.0037	0.9987	1.0049	0.0041
1060	1.0087	1.0046	1.0051	1.0095	1.0034	1.0121	1.0072	0.0034
1065	1.0051	1.0135	1.0200	1.0134	1.0232	1.0162	1.0152	0.0063
1070	1.0043	0.9967	0.9890	0.9952	1.0014	1.0037	0.9984	0.0059
1075	0.9866	0.9875	0.9962	0.9889	0.9909	0.9941	0.9907	0.0038
1080	0.9922	0.9789	0.9885	0.9870	0.9854	0.9922	0.9874	0.0049
1085	0.9904	0.9949	1.0024	0.9903	0.9949	0.9947	0.9946	0.0044
1090	1.0019	0.9916	1.0034	0.9904	0.9935	0.9989	0.9966	0.0055
1095	0.9620	0.9690	0.9733	0.9642	0.9672	0.9555	0.9652	0.0062
1100	0.9958	0.9885	0.9758	0.9755	0.9669	0.9747	0.9795	0.0106
1105	1.0008	0.9758	1.0039	0.9957	0.9939	0.9946	0.9941	0.0098
1110	0.9824	0.9799	0.9628	0.9753	0.9710	0.9831	0.9758	0.0078
1115	0.9977	1.0091	0.9956	1.0015	0.9954	0.9925	0.9986	0.0059
1120	0.9941	0.9869	0.9828	0.9819	0.9835	0.9732	0.9837	0.0068
1125	1.0168	1.0142	1.0109	0.9983	1.0085	1.0015	1.0084	0.0072
1130	1.0242	0.9803	0.9836	0.9852	0.9844	0.9829	0.9901	0.0167
1135	1.0132	0.9992	1.0024	1.0085	1.0055	0.9951	1.0039	0.0065
1140	1.0033	0.9953	0.9911	1.0006	0.9931	0.9864	0.9949	0.0062
1145	1.0063	1.0037	1.0031	1.0067	1.0007	0.9959	1.0027	0.0040
Mean Counts	35105.3	32608.2	31760.7	31226.7	30844.8	29599.9	Mean	0.0072
1 Standard Deviation	407.1	480.9	533.9	496.2	527.3	481.9		
% Standard Deviation	1.16	1.48	1.68	1.59	1.71	1.63		
max./min.	1.043	1.057	1.070	1.067	1.063	1.068		

^a Dosimeter Groups are designated by the number of the first chip in the group.

Table VI-b

Uniformity and Reproducibility of $\text{CaF}_2\text{:Mn}$ Chip Response
(10 Chips per Group)

Dosimeter Group ^a	Dosimeter Group Counts/Mean Counts						Mean	1 Std. Deviation
Test Date:	8/24/81	8/27/81	8/28/81	9/01/81	9/03/81	9/10/81		
1000	1.0015	1.0175	1.0037	1.0190	1.0156	1.0124	1.0116	0.0074
1010	0.9992	1.0123	1.0092	1.0199	1.0209	1.0178	1.0132	0.0082
1020	0.9999	1.0124	1.0093	1.0090	1.0155	1.0126	1.0098	0.0054
1030	0.9941	1.0079	1.0069	1.0079	1.0083	1.0107	1.0059	0.0059
1040	1.0029	1.0119	1.0159	1.0079	1.0117	1.0150	1.0108	0.0048
1050	1.0073	1.0031	1.0086	1.0019	1.0016	1.0077	1.0050	0.0032
1060	1.0065	1.0091	1.0124	1.0114	1.0133	1.0141	1.0111	0.0029
1070	0.9961	0.9921	0.9924	0.9921	0.9961	0.9989	0.9946	0.0028
1080	0.9942	0.9869	0.9952	0.9887	0.9901	0.9935	0.9913	0.0032
1090	0.9816	0.9803	0.9882	0.9773	0.9803	0.9772	0.9808	0.0040
1100	0.9979	0.9821	0.9897	0.9856	0.9804	0.9846	0.9867	0.0063
1110	0.9897	1.0037	0.9821	0.9884	0.9832	0.9878	0.9892	0.0077
1120	1.0051	1.0006	0.9966	0.9901	0.9911	0.9874	0.9951	0.0114
1130	1.0196	0.9897	0.9927	0.9969	0.9949	0.9889	0.9971	0.0114
1140	1.0044	0.9995	0.9969	1.0037	0.9969	0.9911	0.9988	0.0049
Mean Counts	35105.3	32608.2	31760.7	31226.7	30844.8	29599.9	Mean	0.0057
1 Standard Deviation	306.7	388.3	321.5	397.8	418.8	398.3		
% Standard Deviation	0.87	1.19	1.01	1.27	1.36	1.35		
max./min.	1.039	1.038	1.034	1.044	1.041	1.042		

^a Dosimeter Groups are designated by the number of the first chip in the group.

Table VI-c

Uniformity of CAF₂:Mn Chip Response

Date	<u>Groups of 10 Chips</u>		<u>Groups of 5 Chips</u>			
	<u>(From Table VI-b)</u>		<u>(From Table VI-a)</u>		<u>(Corrected for Differences in Related Sensitivity) ^a</u>	
	1 Standard Deviation (%)	Maximum/Minimum	1 Standard Deviation (%)	Maximum/Minimum	1 Standard Deviation (%)	Maximum/Minimum
<u>Preliminary Tests</u>						
8/24/81	0.87	1.039	1.16	1.043	--	--
8/27/81	1.19	1.038	1.48	1.057	1.40	1.070
8/28/81	1.01	1.034	1.68	1.070	1.09	1.064
9/01/81	1.27	1.044	1.59	1.067	0.97	1.046
9/03/81	1.36	1.041	1.71	1.063	0.52	1.019
9/10/81	1.35	1.042	1.63	1.068	0.86	1.029
<u>Quality Control Tests</u>						
10/05/81			1.20	1.056	0.99	1.044
10/15/81			1.66	1.067	0.95	1.043
11/04/81			2.02	1.092	0.98	1.041
11/13/81			2.39	1.099	0.87	1.033
11/24/81			2.87	1.146	0.85	1.041

^a Results of each test were corrected using the relative sensitivity correction factors obtained from the previous test.

Table VI-d

Self-Irradiation/Packaging Test Results

Dosimeter Location	Package Type	Exposure Rate ($\mu\text{R h}^{-1}$)	Mean ($\mu\text{R h}^{-1}$)	Standard Deviation (%)
Environmental Test Chamber	Teflon	16.3	16.4	0.6
	Sealed Teflon	16.6		
	Plastic box	16.4		
	Metal capsule	16.4		
Lead Shield	Teflon	10.9	10.8	3.8
	Sealed Teflon	10.7		
	Plastic box	10.4		
	Metal capsule	11.4		
TLD Reader Room	Sealed Teflon	18.1	18.5	1.9
	Plastic box	18.8		
	Metal capsule	18.4		

Table VI-e

General Experimental Schedule

Preparation (Regimes I, II and III)

- 2:00 PM - Begin placement of chips on annealing tray.
- 2:30 PM - Begin 1 hour anneal at 500°C.
 - Prepare Teflon and plastic packages for storage and irradiation.
- 3:30 PM - Stop anneal, place annealing tray on brass heat sink.
- 3:35 PM - Package chips for irradiation and/or storage.
- 4:00 PM - Perform irradiations (Regime I); repackage irradiated chips in Teflon packages for storage.
- 4:30 PM - Install packaged chips (Regimes I, II and III) in the environmental tests chamber and lead shield, as appropriate.

Preparation (Regime IV)

- 7:00 PM - Begin placement of chips on annealing tray.
- 8:00 PM - Begin 1 hour anneal at 500°C; prepare Teflon packages for storage.
- 9:00 PM - Stop anneal, place annealing tray on brass heat sink.
- 9:05 PM - Package chips in Teflon packages for storage.
- 10:00 PM - Install packaged chips in the environmental test chamber.
- 3:00 PM - Remove Regime IV packaged chips from environmental test chamber and repackage for irradiation.
- 3:15 PM - Irradiate Regime IV chips and repackage for storage.
- 3:45 PM - Re-install Regime IV packaged chips in environmental test chamber.

Readout

- 8:30 AM - Begin placement of calibration chips on annealing tray.
 - 9:00 AM - Begin 1 hour anneal at 500°C of calibration chips.
 - 9:15 AM - Remove packaged chips from the environmental test chamber and lead shield, as appropriate; unpack chips and repackage those to be irradiated (Regime II).
 - 9:30 AM - Perform irradiations of test chips.
 - 10:00 AM - Stop calibration anneal; place annealing tray on brass heat sink.
 - Start preparation of TLD Reader.
 - 10:30 AM - Perform irradiations of the calibration chips.
 - Start readout using interspersed technique.
-

Table VI-f
Assignment of $\text{CaF}_2\text{:Mn}$ Chips

Chip Numbers	Category	Irradiation Status ^a	
1000-1004	A	irradiate before storage	(I)
1005-1009	A	irradiate after storage	(II)
1010-1014	A	no irradiation	(III)
1015-1019	B	irradiate before storage	(I)
1020-1024	B	irradiate after storage	(II)
1025-1029	B	no irradiation	(III)
1030-1034	C	irradiate before storage	(I)
1035-1039	C	irradiate after storage	(II)
1040-1044	C	no irradiation	(III)
1045-1049	D	irradiate before storage	(I)
1050-1054	D	irradiate after storage	(II)
1055-1059	D	no irradiation	(III)
1060-1064	background control		
1065-1069	Regime IV	{ irradiation preceded and followed by storage }	(IV)
1070-1074	"		
1075-1079	"		
1080-1084	"		
1085-1089	"		
1090-1094	"		
1095-1099	"		
1100-1109	calibration control	irradiate before readout	
1110-1119	"	"	
1115-1129	"	"	
1120-1139	"	"	
1125-1149	"	"	
1130-1159	"	"	

^a Roman numerals indicate corresponding Regime.

Table VI-g

Schedule Options Permitting Data Acquisition for 6 StorageIntervals Using 3 Categories of Dosimeters

Day	Activity (P = preparation, R = readout) and Nominal Storage Interval (days)							
0	1,2,3)	P(1,2,5)	P(1,3,6)	P(1,5,6)	P(5,6,7)	P(2,3,7)	P(2,5,7)	P(3,6,7)
1	1) 7)	R(1) P(7)	R(1) P(7)	R(1) P(7)				
2	2) 6)	R(2) P(6)				R(2) P(6)	R(2) P(6)	
3	3) 5)		R(3) P(5)			R(3) P(5)	R(3) P(5)	
5		R(5) P(3)		R(5) P(3)	R(5) P(3)		R(5) P(3)	
6			R(6) P(2)	R(6) P(2)	R(6) P(2)			R(6) P(2)
7					R(7) P(1)	R(7) P(1)	R(7) P(1)	R(7) P(1)
8	5,6,7)	R(3,6,7)	R(2,5,7)	R(2,3,7)	R(1,2,3)	R(1,5,6)	R(1,3,6)	R(1,2,5)

Table VI-h

Uniformity and Reproducibility of LiF Chip Response
(10 Chips per Group)

Dosimeter Group ^a	Dosimeter Group Counts/Mean Counts						Mean	1 Std. Deviation
Test Date:	8/24/81	8/27/81	8/28/81	9/01/81	9/03/81	9/10/81		
100	0.9919	1.0054	0.9986	0.9943	0.9903	1.0030	0.9973	0.0061
110	1.0106	1.0103	1.0134	0.9953	1.0130	1.0066	1.0082	0.0068
120	0.9996	0.9969	1.0067	1.0063	0.9897	0.9970	0.9994	0.0064
130	0.9978	1.0085	1.0049	1.0216	1.0109	0.9969	1.0068	0.0092
140	0.9944	1.0079	1.0224	1.0038	0.9955	1.0104	1.0057	0.0104
150	0.9954	1.0096	1.0145	0.9834	1.0056	0.9873	0.9993	0.0126
160	0.9871	0.9788	0.9829	0.9819	0.9907	0.9988	0.9852	0.0080
170	1.0003	1.0045	0.9984	1.0004	1.0008	0.9942	0.9998	0.0034
180	0.9830	0.9989	0.9816	0.9744	0.9919	0.9978	0.9879	0.0098
190	0.9688	0.9727	0.9616	0.9632	0.9677	0.9651	0.9665	0.0041
200	1.0061	1.0057	0.9937	1.0082	1.0063	0.9969	1.0028	0.0059
210	1.0176	0.9898	0.9969	1.0268	1.0070	1.0184	1.0094	0.0141
220	1.0263	1.0012	1.0191	1.0138	1.0168	1.0159	1.0155	0.0082
230	1.0215	0.9999	0.9995	1.0343	1.0092	1.0065	1.0118	0.0136
240	1.0085	1.0101	1.0056	0.9923	1.0047	1.0051	1.0043	0.0063
Mean Counts	25187.5	25366.9	25102.1	24611.2	24841.5	24405.5	Mean	0.0083
1 Standard Deviation	400.8	289.7	397.8	483.2	312.3	310.7		
% Standard Deviation	1.59	1.14	1.58	1.96	1.26	1.27		

^a

Dosimeter Groups are designated by the number of the first chip in the group.

FIG. VI-a Typical glow curve for a $\text{CaF}_2\text{:Mn}$ chip given an irradiation of 97 mR.

FIG VI-b Composite (computer averages) glow curve for 145 $\text{CaF}_2:\text{Mn}$ chips given an irradiation of 97 mR.

FIG. VI-c Linearity test of $\text{CaF}_2\text{:Mn}$ chips. Error bars indicate 1 standard deviation from the mean of a single chip from the group of 10, and are absent where the data symbol ($\cdot$) covers the area included in 1 standard deviation.

VII. RESULTS AND ANALYSIS

Prior to examining the results of the actual stability experiments, it was necessary to carefully analyze the results of all of the quality control measurements obtained in conjunction with these experiments to verify the integrity of the experimental procedures, protocol and equipment. This chapter therefore begins with analyses of the control data then proceeds with a presentation of the results of the stability tests and detailed evaluations of these results, and concludes with an examination of the results in the context of comparable data available in the literature.

A. TLD Reader Controls

To verify the overall integrity of the data obtained throughout the preliminary experiments and the actual stability experiments, the controls used to determine the stability of the TLD reader itself were examined. These data, for the light source measurements and the LiF control measurements are shown in Figure VII-a. The data are presented in the form of ratios, each measurement having been normalized to the mean of the measurements obtained between September 18 and November 25. (This normalization was chosen because both LiF and light source measurements were available for every readout, September 18 marking the commencement of the stability experiments.) These data show some variation in reader sensitivity; however, these variations are not necessarily unusual. Moreover, both the light source measurements and the LiF measurements indicate the same trend. Table VII-a shows the slopes, intercepts and correlation coefficients for an arbitrarily chosen linear fit. These data

essentially demonstrate that there were no unusual problems with the TLD reader that would jeopardize the results of the preliminary experiments or the stability experiments. It should be emphasized that the absolute change in reader sensitivity is of no consequence to the results of the stability experiments since each measurement was normalized (calibrated) according to the $\text{CaF}_2\text{:Mn}$ controls read out at the same time using the interspersed technique.

B. $\text{CaF}_2\text{:Mn}$ Calibration Controls

As described in Chapter VI, fifty of the one hundred fifty $\text{CaF}_2\text{:Mn}$ chips used for the stability experiments were designated as calibration controls (see Table VI-f). Of these chips, 1145-1149 were irradiated (~100 mR) and read out with every set of readouts, and one group of ten chips from 1100-1139 was irradiated (~100 mR) and read out with each of the four readouts required for a given temperature study. When normalized in the manner applied in the case of the light source and LiF controls, these controls unexpectedly showed an internally inconsistent behavior, the results for chips 1145-1149 being different from those for chips 1100-1139. Further investigation of the data led to a rather interesting discovery. The sensitivity of the 1145-1149 chips appeared to decrease faster than did that of the other controls. To examine this phenomenon more closely, all control data were corrected for reader variation using a correction factor obtained from the light source measurements for the appropriate day and then normalized to the mean value obtained for all one hundred fifty chips in the first uniformity test

(i.e., 35105.3 counts, see Table VI-a). To examine the possibility that the decline in sensitivity might be related to use, (probably due to annealing effects), the results for chips 1145-1149 and chips 1100-1139 were plotted, as shown in Figures VII-b and c respectively, as a function of the number of times used. Indeed, the data reflect similar trends and show a loss of about 15% occurring by the first five uses followed by about 0.6% loss per use thereafter leading to a loss of about 30% after 30 uses. The existence of this phenomenon suggested the need to verify that it was truly independent of any thermal treatments administered throughout the stability experiments. For this purpose analogous data obtained from the uniformity tests for the chips in categories A, B and C and those used for Regime IV (see Table VI-f) were also examined. All of these data are collected in Figure VII-d, substantiating the effect but also its independence of the thermal treatments applied in the stability experiments. It should be noted that in this figure, data for chips read out more than 17 hours after anneal are indicated, since those results also include some fading, as will be shown later, and are not directly comparable to the rest of the data. The important point is that all chips behave similarly, in terms of general loss of sensitivity with use. This phenomenon in no way affects the results of the stability experiments since the chips were handled in such a way that all of them, except 1145-1149 were used the same number of times. Chips 1145-1149 were thus eliminated from consideration as calibration controls and only 1100-1139 were used for direct calibration and normalization of all data in the stability experiments. But while the phenomena is of no direct interest

or consequence to the stability experiments, it nevertheless is of general dosimetric significance. The magnitude of the effect strongly suggests that in the practical use of $\text{CaF}_2:\text{Mn}$ chips in a manner similar to that used here, only dosimeters that have been used the same number of times should be directly compared without considering this phenomenon as a source of error.

C. Quality Control Measurements

As indicated in Chapter VI, four separate measurements were made with each temperature study to verify the integrity and reproducibility of the entire system including the annealing, handling and irradiation of the dosimeters, the entire experimental protocol, the readout procedures and the calibration. For each temperature, the category D chips were used to obtain Regimes I and II data for a storage period of 185 hours in the lead shield at $\sim 20^\circ\text{C}$. The results are shown in Table VII-b. The reproducibility of these data provides a direct empirical method of assessing the expected reproducibility of the entire experimental protocol, except of course for any errors introduced by temperature variations in the environmental chamber, which were estimated to be negligible. The standard deviations of a single measurement from the mean of the five Regime I and II measurements are 1.48% and 1.04% respectively. Two Regime II-type measurements were also made for quality control purposes, one in the lead shield and the other just outside of the environmental test chamber. Since the exposures involved in these measurements were about 2 and 3 mR, approximately two orders of magnitude lower than those involved in the Regime I and II measurements, the observed larger standard devia-

tions, 6.76 and 2.59% (Table VII-b) are appropriate. The precision obtained with these quality control measurements is consistent with what would be expected from propagation of errors based on the preliminary test results and should therefore be representative of the precision of the results of the stability experiments.

D. Stability Test Results

All results from the stability tests are presented in Table VII-c. The interspersed technique was used for all readouts. The data for Regimes I, II and IV were obtained by determining the mean net counts for the chips used for each measurement, subtracting the mean net counts for the chips used for Regime III, and dividing the results by the mean net counts obtained for the calibration control chips. The results for the Regime III dosimeters were subtracted on the basis that whatever happened to them also happened to the rest of the dosimeters and thus had to be subtracted to isolate the effects of interest in Regimes I, II and IV. The Regime III results, containing no exposure from ^{137}Cs , but rather only that due to natural background and self-irradiation, are expressed in terms of exposure rate ($\mu\text{R h}^{-1}$) and were determined by dividing the mean net counts for these chips by the counts per μR determined from the calibration control chips and then dividing the results by the number of hours in the particular storage interval.

The most immediately striking feature in Table VII-c are the results for Regime II, aimed at examining the effects of storage prior to irradiation. Clearly an effect is present but the data indicate no trend as a function of either time or temperature within the ranges tested. This is

further evident from the analysis of these data in Table VII-d, which shows equivalent spreads at any given temperature, or for the average of temperatures, as a function of time and at any given time interval, or for the average of all intervals, as a function of temperature. The equivalent results obtained for the 185 hour storage interval in the lead shield are consistent with the environmental test chamber results. For all thirty data points the mean of 0.9729 with standard deviations from, and of the mean, of 1.67% and 0.3% respectively.

This outcome seems to verify the assumption made in Chapter II that β_R , the trapping efficiency, is independent of thermal history subsequent to TLD preparation, in keeping with the theory of Randall and Wilkins. Nevertheless the data clearly indicate that something occurs to TLD's stored for a period of at least 17 hours between preparation and irradiation that does not occur to the calibration controls i.e., TLD's stored for thirty minutes between preparation and irradiation. If this phenomenon is truly dosimetric in origin, i.e., it somehow affects the trapping efficiency β_R , even though it is independent of time and temperature over the ranges studied, then Equation III-d given in Chapter III for Regime IV should apply. In other words the results for Regime IV storage both before and after irradiation should be a simple combination of the results for Regimes I, storage after irradiation, and II, storage before irradiation, and should be predictable from those data.

Table VII-e shows the comparison between the actual results obtained for Regime IV (from Table VII-c) and those predicted by combining the Regimes I and II results according to Equation III-d. The prediction is

not correct, the mean ratio of the thirty comparisons being 0.975, instead of 1.0, with standard deviations from and of the mean of 3.8% and 0.7% respectively. Rather the predicted values underestimate the measured values by almost exactly the effect observed under Regime II, 0.973. This suggests that the phenomenon observed in Regime II is not dosimetric in origin, i.e., it is unrelated to β_R , the trapping efficiency. Rather it appears to affect TLD's stored for at least 17 hours or more regardless of when irradiation occurs. It therefore seems most likely that the effect manifests itself during readout and is perhaps optically related. If this is the case, then the results for Regimes I and IV should be identical, both incorporating the effect observed in the Regime II experiments. As could be expected from the results in Table VII-e, this is so and is shown in Table VII-f. There appears to be no significant pattern in the comparisons as a function of either time or temperature, and the data over all thirty comparisons show essentially perfect agreement: 1.0037 with a standard deviation of 3.5%. The importance of this is the definite implication that the effect produced in the Regime II experiments holds in all three cases, Regimes I, II and IV, is independent of the time of irradiation as well as of time and temperature, and therefore is most certainly a non-dosimetric effect. Clearly then, the trapping efficiency, β_R , is independent of thermal history.

Since the phenomenon observed in Regime II affects all data, the results for Regimes I and IV first have to be corrected for this effect in order to isolate the expected fading effects for examination. Furthermore, these results can be combined, since they are essentially identical

within statistics, in order to improve precision. The averaged data, divided by 0.9729 to compensate for the Regime II effect, are shown in Table VII-g and are used henceforth in the analysis of Regime I, i.e., fading, effects.

These data are plotted for illustrative purposes in a conventional manner as a function of time in Figure VII-e and as a function of temperature in Figure VII-f. In both cases the data are clearly very smooth functions as might be expected from simple Randall-Wilkins behavior. There is no evidence, at least for the time intervals studied, of the unusual patterns observed by other investigators, Fitzsimmons, for example (Figure IV-b). However, it is obvious that the 'fading' is larger at -25°C than at +20°C. As mentioned in previous chapters, this type of effect has been observed before, especially with other phosphors, and is inconsistent with at least a straightforward (single trap) Randall-Wilkins analysis.

Compliance with the Randall-Wilkins theory can be examined graphically. Having eliminated the effects observed in Regime II and thus isolating only fading, the Randall-Wilkins theory applicable for Regime I can be expressed simply as:

$$I = I_0 e^{-\lambda t} \quad \text{VII-a}$$

where I and I_0 are proportional to n and $(\beta R n_a (\Delta t)_R)$, respectively as given in Equation III-a, and t is the storage interval. Now $\lambda = s \exp (-E/kT)$ so that this equation becomes

$$I/I_0 = \exp [-s \exp(-E/kT)t] \quad \text{VII-b}$$

where I/I_0 is the relative response as given in Table VII-g and Figures VII-e and f. This can be expressed as

$$\ln \left[\frac{-\ln I/I_0}{t} \right] = \ln s - E/kT \quad \text{VII-c}$$

so that a plot of $[(-\ln I/I_0)/t]$ on semi-log paper versus $1/T$ should yield a straight line, if the Randall-Wilkins theory applies, with the slope and intercept yielding the appropriate data for the trap depth, E , and the frequency factor, s , respectively. Figure VII-g shows the data from Table VII-g plotted in this manner. Obviously, the data are inconsistent with the Randall-Wilkins theory at least if a single trap depth is assumed.

The results for Regime III given in Table VII-c have been corrected for the Regime II phenomenon to isolate the effects expected under continuous, constant irradiation and are given in Table VII-h. They are also plotted in a conventional manner as a function of time in Figure VII-h and as a function of temperature in Figure VII-i. These data appear complex as might be expected even from Randall-Wilkins behavior since the fading effects are integrated over the entire storage interval. Immediately suspect and certainly unexplainable initially however are the high exposure rates measured over relatively short intervals for storage at

-25 and +20° C. An exposure rate of ~16 $\mu\text{R h}^{-1}$, and at least less than 20 $\mu\text{R h}^{-1}$ was expected in the environmental test chamber based on preliminary measurements with LiF dosimeters and considering a $\text{CaF}_2\text{:Mn}$ self-irradiation rate in the neighborhood of 9 to 10 $\mu\text{R h}^{-1}$. Nevertheless, the smoothness of the results even at 175°C storage which involved the lowest measured exposures, in addition to the quality control results discussed earlier, argues against any suspicion regarding the credibility of the data.

Compliance with the Randall-Wilkins theory can again be examined graphically however. Having eliminated the effects observed in Regime II to isolate the anticipated integrated fading effects, the Randall-Wilkins theory applicable for Regime III can be expressed as:

$$I = B/\lambda (1 - e^{-\lambda t}) \quad \text{VII-d}$$

where I and B are proportional to n and (B_{Rn_2}) respectively as given in Equation III-c and t is the storage interval. Differentiation and substitution yields

$$dI/dt = B - \lambda I.$$

Therefore a plot of dI/dt versus I, i.e., the exposure rate versus the exposure should produce a straight line if the Randall-Wilkins theory holds with the slope providing the fading factor, λ , and the intercept providing the true exposure rate, B. Figure VII-j shows the data plotted in this manner. The data for 65°, 150° and 175° are close to forming a

straight line but while the exposure rate inferred from the intercepts for the 65° and 150° data are reasonable, that for 175° seems low. The data for -25° and +20° are not conducive to interpretation in this manner.

E. Glow Curve Analyses

Additional information can be gleaned from the glow curves obtained throughout these experiments.

Assuming that at least the behavior during readout is appropriately described by the Randall-Wilkins theory as given in Equation II-c, it is possible to infer information concerning trap depths, frequency factors and kinetic order using the basic glow curve. These parameters are of course of interest because they essentially determine the kinetic behavior of the charge carriers. Figure VII-k shows the composite glow curve for the 145 chips used in the stability experiments given an irradiation of 97 mR for one of the uniformity tests. Since the temperature of the chip is required for some glow curve analyses, an infrascopes*, designed to work with very small target diameters, was used to measure the temperature of the heater pan itself during the readout cycle as well as the temperature of the upper surface of the chip. Lines A and B in Figure VII-k indicate these measured temperatures during the 17 second (500 channels) readout cycle. Since the chip is of finite size, there is a

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Instrument Division, Barnes Engineering Company
30 Commerce Road
Stamford, Connecticut 06902

temperature gradient across the chip at any given instant and thus no single figure for the chip temperature is exactly correct for theoretical purposes. Therefore, when temperature is required in the following analyses, the mean of the pan temperature and that of the upper surface of the chip, as indicated by line C in the figure, is used. Using this approach, the peak occurs at 318°C (591°K).

Three different methods, theoretically precise to varying degrees, were explored for information concerning E, the trap depth. The simplest but also the least exact formula based on the Randall-Wilkins theory is that given by

$$E \sim 25 kT_m$$

where T_m is the peak temperature in degrees Kelvin, k is the Boltzmann constant, and the constant is dependent on the assumption of a frequency factor of $2.9 \times 10^9 \text{ s}^{-1}$, (Randall and Wilkins, 1945). Using the data in Figure VII-k, this formula results in a trap depth of 1.27 eV.

A second approach, (Grossweiner, 1953), requires the use of the temperature corresponding to the peak half maximum as well as to the maximum. In this case the trap depth is approximately given by;

$$E = 1.51 kT_m \frac{T_1}{T_m - T_1}$$

where T_1 is the temperature corresponding to the peak half maximum. This

equation using the peak maximum and half-maximum indicated in Figure VII-k, yields a trap depth of 1.06 eV.

A third method, frequently referred to as the "initial rise method" was developed by Hoogenstraaten (1958). It is based on the fact that the Randall-Wilkins formula, describing the release of trapped charge carriers during readout and given in Equation II-c, is nearly temperature independent as the temperature is raised and the traps begin to empty. At this point the equation reduces to

$$\ln I = E/kT + \text{constant}$$

regardless of the type of kinetics. From this equation it can be seen that a plot of the TL response, I , on a log scale versus $1/T$ should be linear with the slope yielding $-E/k$ from which E can of course be determined. Figure VII-1 shows such a plot derived from the TL response exhibited in the composite glow curve in Figure VII-k. However, this curve is slightly non-linear from the very beginning of the rise, at $1/T \times 10^3 = 2.06$, corresponding to channel 220. Nevertheless, there is no ambiguity about the initiation point of the rise due to the immediate smoothness of the curve starting at that point. For the sake of comparison, the TL response at the peak maximum, channel 341, is 333 counts compared with the response of about 3 counts at the initial rise point. As a result of the non-linearity, the inferred trap depth depends on exactly which portion of the initial rise curve is used. Table VII-i shows that the trap depths calculated using various portions of the curve range from

1.22 to 2.03 eV. Thus the various methods yield trap depth estimates ranging from 1 eV to 2 eV, the former being quite unstable in the Randall-Wilkins scheme, while the latter would be quite stable, all depending of course on the frequency factor, s .

If the Randall-Wilkins formula, as given in Equation II-3, for describing glow curve behavior, is differentiated with respect to temperature and equated to zero, the following equation results

$$\frac{E}{kT_m^2} = -\frac{s}{\alpha} \exp(-E/kT_m)$$

where α is the heating rate. From this equation, the frequency factor, s , can be determined if the trap depth and glow curve maximum peak temperature are known. Using the peak maximum determined from Figure VII-k the frequency factors corresponding to 1 and 2 eV, the range determined above, are $4.2 \times 10^9 \text{ s}^{-1}$ and $2.5 \times 10^{-17} \text{ s}^{-1}$.

With such a wide range of values resulting from the above tests, it is clearly of interest to inquire next about the kinetic order. Halperin and Braner (1960) have provided a criterion for determining the kinetic order based on the symmetry properties of the glow peak. According to their criterion, the kinetics are first order if the symmetry factor

$$\mu < (1-\Delta) \exp(-1)$$

where

$$\Delta = 2 kT_m/E$$

and

$$\mu = \delta_2/\omega$$

where ω is the full width of the glow curve at half maximum and δ_2 is the width at half maximum to the right of a vertical line defining the peak maximum. Based on the glow curve in Figure VII-k, the symmetry factor is 0.465. Using trap depths of 1 and 2 eV, the Halperin and Braner criterion expressed by the above equation yields values of 0.405 and 0.387 respectively indicating that in either case the kinetic order is greater than 1. Now Srivastava and Supe (1979) refer to a method developed by Chen that allows the determination of non-integer kinetic values for kinetic order directly from a curve of symmetry factor versus kinetic order. From that curve, the kinetic order corresponding to the symmetry factor of 0.465 is approximately 1.3.

The results of these tests for trap depth, frequency factor and kinetic order simply support the notion that it is unlikely that the behavior of the $\text{CaF}_2\text{:Mn}$ chips used in these experiments will conform to Randall-Wilkins behavior assuming first or even second order kinetics and assuming a single trap depth.

While the basic glow curve in Figure VII-k, unaffected by any significant fading, can be used in the above ways to examine the basic trapping parameters, the glow curves obtained in the stability experiments can also be examined in a qualitative way to obtain additional clues regarding the phosphor's behavior.

Figure VII-m shows one set of glow curves (each curve is the composite of five chips) obtained for the Regime I and Regime II tests conducted for a storage interval of 185 hours in the lead shield. Already from these room temperature results, it is obvious that there is a slight shift to the right for the glow curve associated with the Regime I, or fading, experiment. This effect is exhibited even more clearly in Figures VII-n and VII-o which contain the glow curves for the Regime IV experiment, i.e., fading results, for all storage intervals at 150°C and 175°C respectively, compared with the standard curve from Figure VII-k. In both cases, the calibration control composite glow curves were essentially identical to the standard composite curve shown. Both figures show the glow curves diminishing in size as a function of storage time and also shifting to the right. The effect can be seen even more dramatically however in Figure VII-p which shows the directly comparable glow curves for Regime I and II, for a storage interval of 161 hours at 175°C along with an expanded version of the Regime I curve, enhanced artificially by means of the HP-85 mini-computer by a factor of five for better comparison with the Regime II curve. It should be pointed out that the Regime II curve is essentially indistinguishable from the calibration control curve or the standard curve from Figure VII-k. The shift in peak temperature for the Regime I curve is obviously significant. The shifts to the right in these figures clearly support the idea suggested by other investigators (e.g., Schulman et al. 1969) that the peak in $\text{CaF}_2:\text{Mn}$ is not the result of a single energy trap but instead the result of a rather broad continuous band of traps. This of course is also consistent with

the rather large range of trap depths derived earlier. The shift exhibited in these curves should not be confused by similar shifts shown by Gorbics et al. (1967) as a result of changes in the heating rate during readout and attributable to thermal quenching effects. Rather, these glow curves were all obtained using the same heating rate and therefore suggest simply a logical more rapid fading of the lower temperature less stable traps in the broad band.

F. Comparison with the Results in the Literature

Considering the paucity of data in the literature (see Chapter IV) for storage temperatures other than room temperature, the only possible comparison is for the latter. The Regime I data from Table VII-g for 20°C easily fall within the data shown from other investigators in Figure IV-k. This of course appears at first to be almost insignificant considering the spread in the data in Figure IV-k. However, the data from the present experiments fit a straight line when plotted in this manner to a remarkably high degree (correlation coefficient 0.818). This suggests an analogous examination of the data obtained for the other storage temperatures. The results are illustrated in Figure VII-q and also indicate an excellent fit to a straight line for all temperatures, essentially supporting a function not of the original single-trap Randall-Wilkins form as given in Equation III-a but rather of the following form,

$$n = (\beta_R n_a (\Delta t)_R) (\alpha \ln t + c) \quad \text{VII-f}$$

where α and c are functions of the storage temperature, T .

While other investigators have plotted their data as a function of the logarithm of time (see Figures IV-b, e, f, h and i), no particular

reason has been advanced for this except perhaps for the convenience of plotting data covering several decades. And while the collected room temperature data of other investigators, as shown in Figure IV-k, seem to offer little support for the validity of the function given in Equation VII-f, the data in Figure VII-q clearly support it. This outcome warrants a further examination of the collection of data in Figure IV-k. As shown in Table IV-a, there is little consistency among the various other investigators with respect to the reference or normalization point used to obtain the data presented in Figure IV-k. However, since a large majority of these investigators obtained data for a storage interval of one hour, it is possible to re-normalize the data in Figure IV-k for most of the investigators relative to their respective one-hour data. This was done and the results are shown in Figure VII-r. The consistency of these data is remarkably good yielding a correlation coefficient of 0.76 when fitted to a straight line. Furthermore, the data obtained in these Regime I experiments (Table VII-g or Figure VII-q) are in excellent agreement with the fitted line. Table VII-j shows that the differences between the Regime I data and those predicted from the fitted line are less than 1% for all but the 41-hour time interval which shows a difference of only 1.57%. The data from Spurny and Kvasnička (1974) indicated with solid triangles in Figures IV-k and VII-r, and shown separately in Figure IV-i, deviate most from the data in Figure VII-r as a whole. Since the phosphor used by Spurny and Kvasnička (see Table IV-a) is unspecified, it can be argued that it might be sufficiently different from that used by the other investigators to make it incomparable. If their data are elimi-

nated from Figure VII-r, the remaining data fit a straight line with a correlation coefficient of 0.83.

The overall agreement of these data, expressed as a linear function of the logarithm of the storage interval for periods ranging from minutes to one year, is particularly significant considering the wide variety of experimental parameters (particularly annealing and readout procedures) used by the several investigators involved (see Table IV-a), and strongly supports the general applicability of the results.

Table VII-a

Trends of TLD Reader Controls During the
Period of the Stability Experiments

	<u>Light Source</u>		LiF Controls Interspersed Throughout Readout
	Measured at the Beginning of Readout	Measured at the End of Readout	
Slope	-0.00081	-0.00092	-0.00087
Intercept	1.24	1.26	1.25
Correlation Coefficient	0.91	0.70	0.83

Table VII-b

Quality Control Measurements Results

Category	Type of Measurement	Mean ^a	Standard Deviation	% Standard Deviation
D - lead shield	Regime I	0.917	0.014	1.48
" " "	Regime II	0.986	0.010	1.04
" " "	Regime III	10.3 $\mu\text{R h}^{-1}$	0.7 $\mu\text{R h}^{-1}$	6.76
Background control outside of environ- mental test chamber	Regime III	17.3 $\mu\text{R h}^{-1}$	0.5 $\mu\text{R h}^{-1}$	2.59

^a Means are comprised of the average of the five measurements each normalized to the calibration control chips readout during the same readout session.

Table VII-c

Summary of Results of the Stability Experiments

Regime	Storage Interval		Storage Temperature (°C)				
	(nominal days)	(exact hours)	-25	+20	+65	+150	+175
<u>Environmental Test Chamber</u>							
I	1	17	0.937	0.958	0.936	0.722	0.485
	2	41	0.911	0.903	0.920	0.635	0.361
	3	65	0.900	0.914	0.894	0.571	0.291
	5	113	0.901	0.907	0.899	0.517	0.205
	6	137	0.880	0.898	0.892	0.506	0.195
	7	161	0.896	0.915	0.890	0.512	0.176
II	1	17	0.960	0.964	0.967	0.963	0.977
	2	41	0.961	0.963	0.974	0.987	0.986
	3	65	0.954	0.965	0.955	1.008	0.969
	5	113	0.937	0.950	0.985	0.969	0.985
	6	137	0.990	0.998	1.003	0.970	0.977
	7	161	0.969	0.979	0.984	0.984	0.953
IV	1,7	17,161	0.875	0.894	0.863	0.473	0.161
	2,6	41,137	0.904	0.919	0.885	0.496	0.185
	3,5	65,113	0.900	0.910	0.899	0.546	0.212
	5,3	113,65	0.899	0.917	0.889	0.590	0.306
	6,2	137,41	0.906	0.921	0.905	0.640	0.379
	7,1	161,17	0.917	0.927	0.910	0.732	0.496
III	1	17	57.3	45.2	15.5	12.5	8.33
	2	41	32.5	29.5	14.1	11.6	7.04
	3	65	19.8	26.0	10.7	12.2	6.33
	5	113	20.7	19.9	15.6	10.7	5.64
	6	137	19.7	20.4	15.6	10.7	5.03
	7	161	18.6	20.1	14.7	9.9	4.93
	8	185	20.3	18.5	16.6	9.3	4.72

Table VII-c (cont'd)

Regime	Storage Interval		Storage Temperature (°C)				
	(nominal days)	(exact hours)	-25	+20	+65	+150	+175
<u>Lead Shield</u>							
I	8	185	0.895	0.918	0.919	0.928	0.927
II	8	185	0.975	0.978	0.992	0.999	0.983
III	8	185	10.1	9.6	9.8	11.2	10.9

Notes:

Regimes I, II and IV results are normalized to calibration control results.

Regime III results are expressed in units of exposure rate ($\mu\text{R h}^{-1}$).

Regime IV storage intervals show the intervals before and after irradiation.

All lead shield results were obtained for storage at $\sim 20^\circ\text{C}$ but simultaneously with the results for the environmental test chamber temperatures indicated.

Table VII-d

Analysis of the Results of Regime II Experiments

<u>Storage Interval</u> (nominal days)	<u>Storage Temperature (°C)</u>					<u>1 Standard</u>		<u>% Standard</u> <u>Deviation</u>
	-25	+20	+65	+150	+175	Mean	Deviation	
1	0.960	0.964	0.967	0.963	0.977	0.966	0.007	0.69
2	0.961	0.963	0.974	0.987	0.986	0.974	0.012	1.24
3	0.954	0.965	0.955	1.008	0.969	0.970	0.022	2.28
5	0.937	0.950	0.985	0.969	0.985	0.955	0.021	2.22
6	0.990	0.998	1.003	0.970	0.977	0.988	0.014	1.41
7	0.969	0.979	0.984	0.984	0.953	0.974	0.013	1.34
Mean	0.962	0.969	0.978	0.980	0.974	0.972	0.0073	0.75
1 Standard Deviation	0.017	0.017	0.017	0.016	0.012	0.008		
% Standard Deviation	1.81	1.72	1.69	1.67	1.23	0.83		

Table VII-e

Comparison of Predicted and Measured Regime IV Results ^a

Nominal Storage Intervals before, t_i , and after, t_j , Irradiation (days,days)	Storage Temperature (°C)					Mean	1 Standard Deviation
	-25	+20	+65	+150	+175		
1,7	0.9825	0.9869	0.9976	1.0425	1.0698	1.0164	0.0378
2,6	0.9365	0.9404	0.9821	1.0065	1.0351	0.9801	0.0424
3,5	0.9549	0.9612	0.9548	0.9540	0.9373	0.9524	0.0089
5,3	0.9367	0.9466	0.9900	0.9373	0.9376	0.9496	0.0229
6,2	0.9950	0.9408	1.0200	0.9631	0.9279	0.9694	0.0381
7,1	0.9896	1.0118	1.0119	0.9701	0.9334	0.9834	0.0329
Mean	0.9658	0.9646	0.9927	0.9789	0.9735	0.9751	0.0114
1 Standard Deviation	0.0265	0.0290	0.0232	0.0387	0.0622	0.0245	

^a

Note:

$$\frac{\text{Predicted IV } (t_i, t_j)}{\text{Measured IV } (t_i, t_j)} = \frac{\text{Measured I } (t_i) \times \text{Measured II } (t_j)}{\text{Measured IV } (t_i, t_j)}$$

Table VII-f

Comparison of Regime I Results with Regime IV Results^a

Nominal Storage Intervals before, t_i , and after, t_j , Irradiation (days, days)	Storage Temperature (°C)					1 Standard	
	-25	+20	+65	+150	+175	Mean	Deviation
1,7	1.0238	1.0235	1.0312	1.0824	1.0947	1.0511	0.0346
2,6	0.9741	0.9766	1.0087	1.0198	1.0508	1.0060	0.0320
3,5	1.0006	0.9963	1.0001	0.9463	0.9675	0.9822	0.0243
5,3	0.9999	0.9963	1.0052	0.9676	0.9516	0.9840	0.0234
6,2	1.0051	0.9804	1.0171	0.9925	0.9503	0.9891	0.0257
7,1	1.0219	1.0331	1.0281	0.9865	0.9792	1.0098	0.0250
Mean	1.0042	1.0010	1.0151	0.9991	0.9990	1.0037	0.0067
1 Standard Deviation	0.0181	0.0228	0.0126	0.0477	0.0597	0.0259	

^a
Note:

$$\frac{\text{Regime I Results}}{\text{Regime IV Results}} = \frac{\text{Measured I } (t_i)}{\text{Measured IV } (t_j)}$$

Table VII-g

Revised Regime I Results ^a

<u>Storage Interval</u> (nominal (exact days) hours)		<u>Storage Temperature (°C)</u>				
		-25	+20	+65	+150	+175
1	17	0.953	0.969	0.949	0.747	0.504
2	41	0.934	0.938	0.938	0.656	0.381
3	65	0.925	0.941	0.916	0.597	0.307
5	113	0.926	0.934	0.924	0.546	0.215
6	137	0.917	0.934	0.913	0.515	0.195
7	161	0.910	0.930	0.901	0.507	0.173

^a

Note:

$$\text{Results} = \frac{\text{Measured I (t}_j\text{)} + \text{Measured IV (t}_j\text{)}}{2} \times \frac{1}{0.9719}$$

Table VII-h
Revised Regime III Results ^a

<u>Storage Interval</u>		<u>Storage Temperature (°C)</u>				
(nominal days)	(exact hours)	-25	+20	+65	+150	+175
1	17	58.9	46.5	15.5	12.8	8.56
2	41	33.4	30.3	14.5	11.9	7.24
3	65	20.4	26.7	11.0	12.5	6.50
5	113	21.3	20.5	16.0	11.0	5.79
6	137	20.2	20.9	16.0	10.7	5.17
7	161	19.1	20.7	15.1	10.2	5.07
8	185	20.9	19.0	17.1	9.56	4.85

^a

Note:

Results - $\frac{\text{Measured III}}{0.9729}$

Results are in units of $\mu\text{R h}^{-1}$.

Table VII-i

Trap Depths Determined Using the Initial Rise Method

Band Considered ($1/T \times 10^3$, °K)	Number of Data Points	Correlation Coefficient ^a	Trap Depth (eV)
2.040 - 2.001	12	0.996	2.03
2.001 - 1.961	14	0.997	1.59
1.961 - 1.921	13	0.998	1.43
1.921 - 1.881	14	0.999	1.22

^a Fit to a straight line.

Table VII-j

Regime I Results Compared with Those of Other
Investigators

Storage Interval (hours)	Measured Results ^a	Calculated Results ^b	Percent Difference ^c
17	0.969	0.963	+ 0.62
41	0.938	0.953	- 1.57
65	0.941	0.948	- 0.74
113	0.934	0.942	- 0.85
137	0.934	0.939	- 0.53
161	0.930	0.938	- 0.85

^a From Table VII-g.

^b Inferred from a least-squares straight line fit
to the data shown in Figure VII-q.

^c Percent Difference = $\frac{\text{Measured} - \text{Calculated}}{\text{Calculated}} \times 100$

FIG. VII-a TLD Reader control data normalized to the mean values obtained between September 18 and November 25.

Fig. VII-b Results for $\text{CaF}_2:\text{Mn}$ control chips, 1145-1149 corrected for reader variation and normalized to that obtained from the initial uniformity test, as a function of the number of uses.

Fig. VII-c Results for $\text{CaF}_2\text{:Mn}$ control chips, 1100-1139, corrected for reader variation and normalized to that obtained from the initial uniformity test, as a function of the number of uses.

Fig. VII-d Results for $\text{CaF}_2\text{:Mn}$ control chips, category A, B, C chips and Regime IV chips, corrected for reader variation and normalized to those obtained from the initial uniformity test, as a function of the number of uses.

Fig. VII-e Regime I (fading) results (relative response), from Table VII-g as a function of storage time.

Fig. VII-f Regime I (fading) results (relative response), from Table VII-g as a function of storage temperature.

Fig. VII-g Regime I (fading) results, from Table VII-g plotted to test compliance with the Randall-Wilkins theory (Eq. VII-c).

FIG. VII-h Regime III results, from Table VII-h, as a function of storage time.

Fig. VII-i Regime III results ($\mu\text{R h}^{-1}$), from Table VII-h, as a function of storage temperature.

Fig. VII-j Regime III results ($\mu R h^{-1}$), from Table VII-h plotted to test compliance with the Randall-Wilkins theory (Eq. VII-e).

FIG. VII-k Composite glow curve obtained from a uniformity test of the 145 chips used in the stability experiments given an irradiation of 97 mR.

FIG. VII-1 The initial rise, or TL response, of the beginning of the glow curve in Fig. VII-k, according to the method of Hoogenstraaten.

FIG. VII-m Glow curves obtained for chips stored for 185 hours at room temperature before (Regime II, curve A) and after (Regime I, curve B) an irradiation of 97 mR.

FIG. VII-n Glow curves obtained for chips stored at 150°C after (Regime I) an irradiation of 97 mR for intervals of 17, 41, 65, 113, 137 and 161 hours (curves B,C,D,E,F and G, respectively) compared with the 145-chip composite glow curve for a uniformity test, from Figure VII-k, (curve A).

FIG. VII-o Glow curves obtained for chips stored at 175°C after (Regime I) an irradiation of 97 mR for intervals of 17, 41, 65, 113, 137 and 161 hours (curves B,C,D,E,F and G, respectively) compared with the 145-chip composite glow curve for a uniformity test, from Figure VII-k, (curve A).

FIG. VII-p Glow curves obtained for chips stored for 161 hours at 175°C before (Regime II, curve A) and after (Regime I, curve B) an irradiation of 97 mR, and curve B computer-enhanced by a factor of five.

Fig. VII-q Regime I, (fading) results (relative response) from Table VII-g fitted to a straight line (as a function of storage time) in the form of Eq. VII-f; R^2 is the correlation coefficient.

FIG. VII-r Fading results of other investigators taken from Fig. IV-k and normalized to the respective one-hour results. See Table IV-a for the legend, '*' indicates the normalization point for all data.

VIII. CONCLUSIONS

Experiments have been carried out with $\text{CaF}_2:\text{Mn}$ to investigate in a controlled and comprehensive manner, the applicability of the Randall-Wilkins theory for describing the behavior of this TLD material especially under conditions encountered in the common practice of thermoluminescence dosimetry. The experiments were designed to allow the isolation of effects occurring prior to irradiation, after irradiation and during irradiation. Basically, the results of the stability experiments suggest the following conclusions for the time intervals and temperatures studied:

- 1) There is no evidence of any temperature- or time-related phenomena that affect the phosphor between preparation and irradiation, and hence influence sensitivity. In other words it appears that the trapping efficiency is constant and independent of temperature, a result not inconsistent with the Randall-Wilkins theory but only in the sense that it is an assumption made in the derivation of that theory.
- 2) There clearly exists some phenomenon which causes an approximate 3% decrease in TL response if the phosphor is stored at least 17 hours, prior to, after, and presumably during, irradiation. Since the effect is independent of the time of irradiation, it is unlikely to be dosimetric in nature and is more likely to be an optically-related phenomenon.
- 3) Fading takes place but certainly cannot be described by the Randall-Wilkins theory assuming a single trap. Rather, the

fading at each temperature is a linear function of the logarithm of the storage time (17 to 161 hours) following irradiation.

When carefully analyzed, the data of other investigators, extending from storage periods of a few minutes up to one year, interpreted uniformly with respect to normalization, are clearly in agreement with these results.

- 4) It appears that some additional effect occurs when the phosphor undergoes continuous irradiation, but the exact nature of the effect cannot be discerned from the results of these experiments.
- 5) Glow curve results and analyses clearly support the notion, already advanced by some earlier investigators, that this phosphor contains not a single trap, but most likely a band of several, probably many, traps somewhere between 1 and 2 eV.

Peripheral results indicate that the material studied suffers a fairly rapid decrease in sensitivity with use, a phenomenon presumably associated with annealing effects. Further, at least this manufacturing batch of chips is contaminated, resulting in self-irradiation equal to or exceeding the exposure rate typical of the natural radiation background in the United States. Both of these problems require careful attention for practical applications.

From a theoretical point of view, the results clearly do not support the Randall-Wilkins theory, assuming a single trap. Rather, the fading results for room temperature, obviously in agreement with analogous (interpretable) data in the literature, can be described as a function of the logarithm of the storage time. Furthermore, this function is

unquestionably supported by the fading results obtained for the temperatures studied other than room temperatures, and for which no other equivalent comprehensive body of data was found in the literature. While evidence from the analyses of the glow curves supports the idea that the apparently single trap of $\text{CaF}_2:\text{Mn}$ is rather a band of traps, suggesting that the Randall-Wilkins theory may still hold assuming a combination of traps, possible re-trapping and perhaps, trap conversion or transfer, the overall experimental results preclude this interpretation. This is the case since, in no way, can Randall-Wilkins type fading, based on a loss of signal essentially described by $\exp(-E/kT)$, (i.e., a loss that increases as the temperature increases) explain the fact that the results obtained for storage at $+20^\circ\text{C}$ show less fading than do the results for storage at -25°C . Due in part to the obvious complexity of the trap structure, it is impossible to determine the significance of the logarithmic function to which the experimental results conform, based solely on the data thus far available. Further explanation will certainly require at least additional experimental work, probably at high storage temperatures, specifically directed at examining the temperature dependence of the coefficients of this function.

From a practical point of view, the results of these experiments clearly indicate that for the common applications such as environmental, personnel and medical dosimetry, usually conducted under conditions within the -25°C to $+65^\circ\text{C}$ range, $\text{CaF}_2:\text{Mn}$ performs in a totally acceptable and predictable manner with respect to stability. It should be noted however that one exception may be the rather interesting and as yet unexplained

behavior exhibited in the Regime III (continuous and simultaneous irradiation and storage) experiments for relatively short time intervals at -25°C and $+20^{\circ}\text{C}$. These effects obviously warrant further investigations especially at higher irradiation rates and over time intervals on the order of hours in order to improve precision, minimize any results associated with self-irradiation and, most importantly, to establish whether or not they are dosimetric in origin.

There are unquestionably some remaining problems requiring attention before thorough understanding of the behavior of $\text{CaF}_2:\text{Mn}$ as a TLD is achieved. However this research has revealed a clear functional relationship for the behavior of $\text{CaF}_2:\text{Mn}$ and demonstrated that this phosphor has highly favorable stability properties for common, wide-spread practical application.

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