THERMOLUMINESCENCE RESPONSE OF LiF TO X- AND GAMMA RAYS; A STUDY OF RATE AND ENERGY DEPENDENCE OVER A WIDE RANGE OF EXPOSURES

MARGARETE EHRLICH
National Bureau of Standards, Washington, D.C.

Abstract—The total thermoluminescence light emission ("response") of LiF (TLD grade) was studied as a function of exposure and exposure rate, and as a function of photon energy. ^{60}Co gamma rays and a broad spectrum of low-energy bremsstrahlung were employed. No rate dependence of the response was detected over the entire range of exposures and exposure rates employed (from about 10^2 R to 2×10^7 R, and from about 10^2 R/h to 7×10^6 R/h, respectively). This represents further evidence that centers other than F centers are involved in the thermoluminescence of LiF (TLD grade).

A comparison of the curves of response versus exposure for the two photon spectra confirms Naylor's findings that the superlinearity region is steeper for ^{60}Co gamma radiation than for low-energy X-rays, and reveals that the effect is indeed dependent on photon energy rather than on exposure rate. These findings are compatible with an explanation of superlinearity as being due to the formation of additional traps by the radiation proper. For exposures above those causing superlinearity, the difference in curve shape again disappears. Also, there is no dependence on energy of the location and height of the response maximum, which suggests that the inhibiting mechanism is independent of photon energy.

INTRODUCTION

Most of the work reported in the literature on the influence of exposure rate (or absorbed-dose rate) and photon energy on the thermoluminescence of LiF (TLD grade) was done over a limited range of total exposure (or dose). Karzmark *et al.*,[1] for example, established the absence of rate dependence over a rate range from about 500 to 2×10^8 rads/sec at three levels of absorbed dose lying between 15,000 and 25,000 rads. More recently, Tochilin and Goldstein[2] employed exposure levels between about 1300 and 5000 R, but not any two of them at the same rate, and found no rate dependence up to 2×10^{11} R/sec. Many authors publishing data on the energy dependence of the thermoluminescence of LiF do not even indicate at what exposure level the data were obtained.[3,4] Frequently, a single exposure level falling in the linear region of the response curve is investigated. A notable exception to this practice is the work of Naylor[5] who studied the shape of the thermoluminescence-response curve* over a total absorbed-dose range from below 50 to around 1000 rads for photons of energies between about 30 keV and 1 MeV. He found that, at the 50-rad level, the response of ConRad "N" LiF powder to bremsstrahlung of an effective energy of 130 keV is more than 110% of that to ^{60}Co gamma radiation, while, at the 800-rad level, it is less than 90% of the ^{60}Co response. He concluded from these findings that, since, in the light of the current theory, superlinearity is due to the formation of new traps, ^{60}Co gamma radiation is considerably more effective in producing new traps in the range from 50 to 800 rads than is 130-keV X-radiation. Naylor found the same effect to exist also in Harshaw TLD-100 powder, but to a lesser degree. No mention is made in his

* Throughout this paper, the terms "thermoluminescence-response curve" and "response curve" are used to designate the curve obtained by plotting the area under the glow curve as a function of exposure.

my time in considering some general issues relating to personnel monitoring policy.

Several papers in this session have been devoted to showing that in many situations TLD produces results as good as or better than film badges. For the measurement of the dose at a point on the surface of the body lithium fluoride certainly takes some beating. However, the film badge does other things besides measuring the dose at a point. It can define the type of radiation giving rise to the dose, whether the radiation is entering or leaving the body at the point of measurement and, when large numbers are involved, the film badge can give results more quickly and more cheaply than lithium fluoride. On the other hand we have seen that for measuring doses to the fingers or the hand the film badge is almost worthless compared with sachets of lithium fluoride or Teflon-LiF discs. A strong case has also been made for using calcium fluoride devices as integrating dosemeters, or as alternatives to quartz fibre dosemeters (although they have not the self-reading facility of the latter); and of course equally strong claims have been made for radio-photoluminescent glass as the basis of a suitable integrating dosemeter. It would seem, therefore, that in view of all these developments in the dosimetry field, the time is not ripe for taking up prepared positions in the defence of either the film badge, TLD, glass or any other system for personnel monitoring. In my view a flexible policy is the correct one in present circumstances—one which allows plenty of opportunity for experimental and operational trials.

Developments I should like to see reported at the second I.R.P.A. Conference would include the following:

(i) Further work on solid TL systems along the lines of the LiF single crystals discussed by Cameron;
(ii) Automation to simplify and speed up the read-out procedures;
(iii) Investigations into other TL materials having fewer idiosyncracies than LiF and cheap enough to throw away after read-out (e.g. lithium borate, which sells at 1*d.* per dosemeter);
(iv) Further work on TL methods for personnel monitoring of fast neutrons;

and, perhaps only obliquely concerned with thermoluminescence,

(v) Consideration by I.C.R.P. of alternative methods of specifying maximum permissible doses for external irradiation, in terms of the dose at the surface of the body. This would resolve the present difficulty whereby personnel dosemeters must also take on the characteristics of a simple spectrometer.

note of the dose rates used in the experiments. If the dose rates were different for the different energies, the observed phenomenon could be due just as well to a variation of curve shape with the rate of energy absorption by the LiF crystal lattice, regardless of photon energy.

The work reported here, which had been conceived before Naylor's note was published, deals with the shape of the LiF (TLD) response curve obtained with photons at different exposure rates and photon energies, with emphasis on the regions of non-linear response. Non-linearity in the response-versus-exposure curve points to either a multiple-stage process or a change in the relative importance of two competing processes. Therefore, shape changes with exposure rate and photon energy are most likely to occur in the non-linear regions of the curve, if at all, i.e. in the "superlinearity" region and the region in which the response curve goes through a maximum.

STATUS OF THEORY

Nature of thermoluminescence centers. Morehead and Daniels exposed LiF crystals to different types of ionizing radiation and studied the resulting thermoluminescence, and the formation and destruction of F centers and their composites.[6] They found the energy required for F-center formation to be different for different types of radiation, and to increase with the total dose delivered. They showed that both the thermal and optical bleaching characteristics of LiF depend on the type of radiation employed, and that, in fact, two LiF crystals exposed to different types of radiation have different types of glow curves, even when they contain the same concentration of F centers. This indicates that, for LiF (TLD grade), a simple F-center theory of thermoluminescence does not suffice. Recently, Claffy reported[7] that the concentration of impurities in the LiF, in particular the concentration of the Mg ions present, determines the shape of the absorption bands of the resulting centers, and also the glow curves. Thus it seems that the thermoluminescence may be due in part to the impurity centers.

The role of lattice damage in the superlinearity region. A further puzzling phenomenon in the thermoluminescence of LiF (TLD grade) is the presence of the "superlinearity" region of the response curve. Cameron *et al.*[8] developed a theory explaining the enhanced thermoluminescence in this region by the assumption that, above a ^{60}Co exposure level of about 2000 R, new electron traps are created by the radiation proper.

A study of the shape of the response curve in the superlinearity region as a function of photon energy could furnish a clue as to whether or not new trap formation is important. Since the probability both for direct lattice-ion displacement by the incident radiation and for the formation of new vacancies at dislocations should decrease with decreasing radiation energy, a decrease in superlinearity with decreasing radiation energy would be compatible with formation of new traps.

Thermoluminescence inhibition. For the segment of the thermoluminescence response curve close to its maximum, Morehead and Daniels[6] obtained information on curve shape as a function of the type of the incident radiation. They found considerable difference in curve shape, as well as a difference in the location and height of the response maximum, the radiation depositing the largest amount of energy for a given interaction producing the highest response maximum. They explained this effect by the greater ability of radiation depositing large amounts of energy per interaction to produce new traps and thus a higher saturation concentration of F centers.

EXPERIMENTAL TECHNIQUE

Sources. A commercial kilocurie ^{60}Co therapy source and two water-shielded kilocurie ^{60}Co sources were used to provide six different exposure rates between about 10^2 and 7×10^6 R/h. Both sources had been calibrated previously with suitable cavity-ionization chambers. Low-energy bremsstrahlung was furnished by a commercial 250 kV constant-potential X-ray machine, modified to provide precision regulation of voltage and current. The X-ray machine was operated at 200 kV constant potential, with inherent filtration only (HVL about 5 mm Al). The exposure rate at the position of the samples was about 7×10^3 R/h. Space did not permit a variation of X-ray exposure rates over a large enough range to warrant the effort, and variation of rates through adding of filtration was decided against, because of the associated change in spectral shape. A calibrated Victoreen R-meter was used to determine the X-ray exposure rate. All exposures are estimated to have been accurate to within 3%.

Choice and treatment of LiF powder. Most of the experiments were done with Harshaw LiF, TLD-100 powder, of batch DW-48. Some were performed with both TLD-100 and TLD-700 powders. Yet, since the results were qualitatively similar for both types of powder, only the TLD-100 results will be discussed here. All powder was annealed prior to exposure for 15 min at 400°C, and was exposed in hard polyethylene vials of 3 mm i.d. and 1 mm wall thickness. Plastic sleeves were provided around the vials for electronic equilibrium at ^{60}Co photon energies. All powder was stored in the dark in air-conditioned rooms. Before the "readings", the powder samples were heated in their vials for 15 min at 100°C, in order to empty possibly filled shallow traps.

Readout procedure. A commercial powder dispenser, whose operation was found to be reproducible to within $1\frac{1}{2}$% standard deviation, was used to fill the heating cup of a commercial thermoluminescence "reader". Each polyethylene vial contained sufficient powder for two individual reading samples. The particular reader employed permitted simultaneous recording of glow curves and readout of "integral counts". With suitable precautions (such as a sufficient waiting period between readings to bring the temperature of the heating pan down close to room temperature each time), individual readings obtained on simultaneously exposed powder samples with a given photomultiplier setting in any one readout session, could be made to agree to within 3%. Below the region of thermoluminescence inhibition, the number of integral counts proved to be proportional to the height of the glow peaks to within 5%.

In order to cover the required five decades of thermoluminescence intensities, the photomultiplier gain had to be changed during the reading sessions. Since the high exposure range necessitated readout with photomultiplier voltages between only 500 and 1000 V, the weak light source provided with the "reader" as a constancy check could not be used. Instead, gain ratio and gain constancy checks had to be provided by a determination of photomultiplier voltages obtained in the readout of identically exposed powder samples. Whenever possible, inaccuracies due to variations in reader performance were avoided by reading all powder samples belonging to a particular phase of the experiment on the same day. This caused the period between exposure and reading to vary between about one and ten days. No corrections for image fading or growth were made, since the variations of response with time between exposure and reading were within the limits of over-all experimental accuracy. The readings for the various individual phases of the rate-dependence experiment which, in some instances, were obtained weeks apart, were scaled at suitable overlapping tie-in points.

RESULTS OF EXPERIMENTS AND CONCLUSIONS

Rate dependence. Figure 1 is a plot of integral counts as a function of exposure to ^{60}Co gamma rays at the three rates obtained with the water-shielded sources (range from below 5×10^3 to above 7×10^6 R/h). Also shown, at selected exposure levels, are samples of glow curves (total counts versus temperature, not to scale). One curve suffices at any one level, since there is no significant change in curve shape with exposure rate. In order to avoid further scaling and the resulting further inaccuracies, the data obtained with the therapy sources (exposure rate range from about 100 to 2600 R/h) are not shown on this figure, but are included in Fig. 2, where they are compared with the 200-kV data obtained during the same experimental phase. (See the following section on energy dependence for a full discussion of Fig. 2.) It was physically impossible to overlap the rates used with the two types of ^{60}Co sources. Yet, the lowest rate obtained with the water-shielded sources (Fig. 1) is less than a factor of two higher than the highest rate obtained with the ^{60}Co gamma-ray therapy sources (Fig. 2).

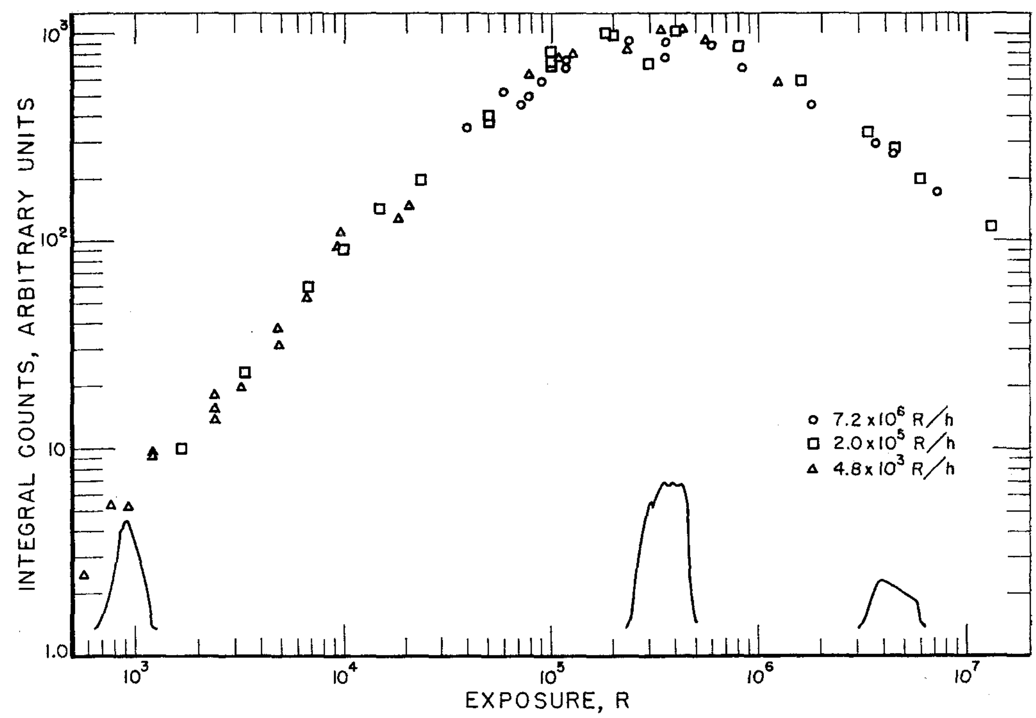

FIG. 1. Rate dependence study with ^{60}Co gamma radiation (water-shielded sources). Circles: 7.2×10^6 R/h. Squares: 2.0×10^5 R/h. Triangles: 4.8×10^3 R/h. At selected exposure levels, samples of glow curves (total counts versus temperature) are included (not to scale).

The continuity provided in this way is considered adequate.

The spread of the individual data points obtained with the water-shielded sources at different reading sessions for any one exposure and exposure rate is seen to be about $\pm 15\%$, even after scaling, at least in the ascending portion and at the maximum of the response curve shown in Fig. 1, and does not seem to vary with exposure level. The spread in the data points is considerably less in Fig. 2, and also in Fig. 1 in the region of decreasing response, for which the data were obtained in a single reading session. Yet, the over-all imprecision probably is still around 10%. Within these rather wide limits of experimental imprecision, no change in the shape of the response curve is detected over the exposure-rate range from about 100 to 7×10^6 R/h for exposures lying between about 10^3 and 2×10^7 R. Inasmuch as Karzmark[1] established the absence of rate dependence at the 20,000 R level within about 5% or better, over a range of exposure rates overlapping the range covered here, and inasmuch as the present data show no trend with rate over the entire response range, there is reason to believe that the thermoluminescence response is, indeed, essentially independent of exposure rate over the entire range covered. This result could be of importance for the theory of thermoluminescence in LiF (TLD grade), since Mitchell *et al.*[9] have shown F-center formation to be dependent on exposure rate, at least in one of the alkalihalides (KCl). It is planned to study the coloration of LiF (TLD grade) as a function of exposure rate over the same range of rates and total exposures over which thermoluminescence has been found to be independent of rate. Rate dependence of the coloration would be conclusive evidence

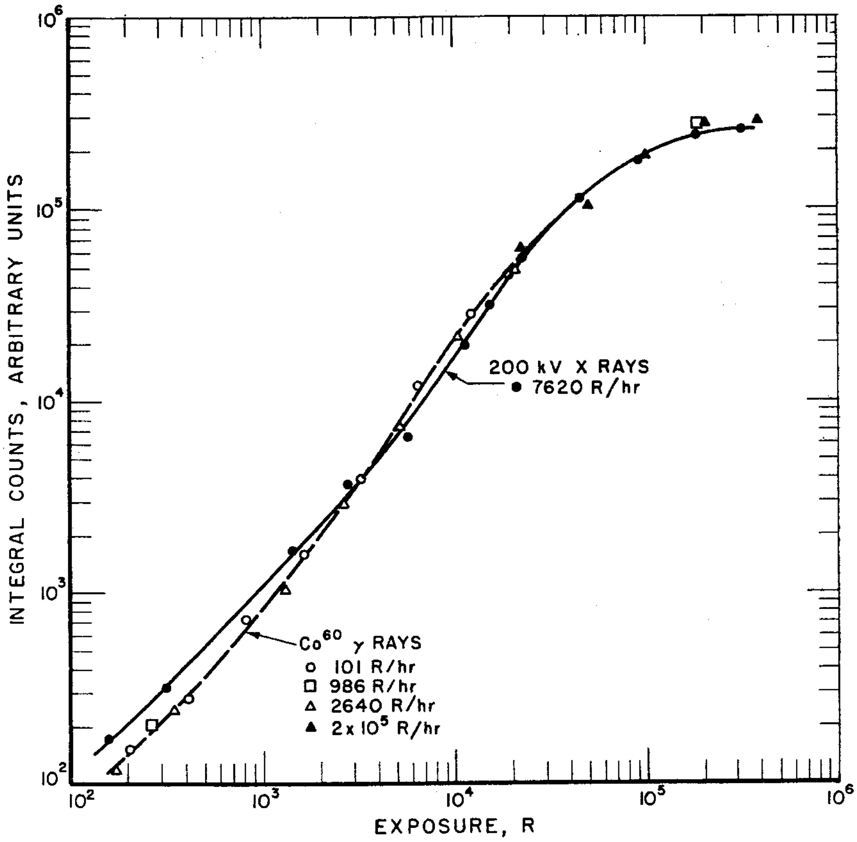

FIG. 2. Energy-dependence study, and rate-dependence study with ^{60}Co gamma radiation (therapy sources). Filled-in circles: 200 kV X-radiation, 7620 R/h. Open circles: ^{60}Co gamma-radiation, 101 R/h. Squares: ^{60}Co gamma radiation, 986 R/h. Open triangles: ^{60}Co gamma-radiation, 2640 R/h. Filled-in triangles: ^{60}Co gamma radiation, 2×10^5 R/h water-shielded source), repeated from Fig. 1, and fitted at about 2×10^4 R.

that F centers do not play an essential role in the thermoluminescence of LiF (TLD grade).

Energy dependence. Figure 2 is a plot of integral counts versus exposure to ^{60}Co gamma-ray photons and to low-energy X-ray photons. The curve shape suggested by the few data points below around 350 R for both photon-energy regions, is consistent with the linear response usually found in this exposure range. Yet, for the ^{60}Co gamma rays, superlinearity sets in above around 350 R, while, for low-energy X-ray exposures, the response remains linear to about 2000 R. The superlinearity region is clearly steeper for ^{60}Co gamma rays than for the low-energy X-radiation.* Above 20,000 R, the curves again have the same slope.

These findings confirm Naylor's results for low exposures[5] and extend them to higher exposure levels. They also reveal that the difference in slope of the response curve to two

* Inasmuch as the relative response to the two different types of radiations depends upon the difference in attenuation for different sample geometries, locations of the two curves obtained with different photon energies (in particular, the fact that they cross) is fortuitous. The only fact of importance is the difference in their slope.

different types of radiation is not due simply to a difference in exposure rate, but truly to a difference in the photon energy, as was assumed by Naylor. In the light of the introductory discussions, the findings are compatible with new trap formation as the cause of superlinearity.

Another interesting result is that the difference in curve slope disappears as the response maximum is approached. In fact, there does not seem to be an appreciable difference in the height and peak of the response maximum for the two types of radiation—a result that is unexpected, particularly considering the findings of Morehead and Daniels.[6] It is planned to extend the study of the region of maximum response to other types of radiation, in order to check these findings over a wider range of energy deposit per interaction.

ACKNOWLEDGEMENT

The author is grateful to Dr. Harold O. Wyckoff for his sustained interest and encouragement, and his helpful suggestions.

REFERENCES

1. C. J. Karzmark, John White and J. F. Fowler. *Phys. in Med. and Biol.* **9,** 273 (1964) and private communication.
2. E. Tochilin and N. Goldstein. USNRDL-TR-939, December 1965. N. Goldstein. Private communication.
3. J. R. Cameron, F. Daniels, Noye Johnson and G. Kenney. *Science* **134,** 334 (1961).
4. B. E. Bjärngard, R. McCall and I. A. Berstein. *Proc. First International Conference on Medical Physics*, Harrogate, England, 1965.
5. G. P. Naylor. *Phys. in Med. and Biol.* **10,** 564 (1965).
6. F. F. Morehead and F. Daniels. *J. Chem. Phys.* **27,** 1318 (1957).
7. E. Claffy. *Proc. International Conference on Luminescence Dosimetry*, Stanford, California, 1965; U.S.AEC (1967).
8. J. R. Cameron, D. W. Zimmerman and R. W. Bland. *Proc. International Conference on Luminescence Dosimetry*, Stanford, California, 1965; U.S.AEC (1967).
9. P. V. Mitchell, D. S. Wiegand and R. Smoluchowski. *Phys. Rev.* **121,** 484 (1961).