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T. G. Stoebe* and S. Watanabe

1 – INTRODUCTION

Considerable progress has been made in recent years in the characterization of the thermoluminescent (TL) behavior of lithium fluoride. After it was found that purified LiF gave poor TL response, it was determined that the impurity magnesium was necessary for high TL sensitivity[12,22,70]. Further. it was found that Mg-doped LiF did not always give the same luminescent yield, due to the presence in some samples of additional impurities which are also needed for high TL sensitivity. The standard LiF (TLD-100) material developed by the Harshaw Chemical Co.** therefore contains a major amount of Mg and minor amounts of other impurities, including Al, Ti, and Eu[60]. More recent work has shown that titanium is the most important of these additional impurities, being related to the luminescence (light emission) process in this material[67,68,93]. Thus the impurity concentrations of importance in LiF (TLD-100) are the 200 ppm Mg and the 15 ppm Ti[68,94] present in the material.

LiF (TLD-100) must be standardized for re-use by a pre-irradiation heat treatment[12,27,94] consisting of annealing the material for 1 h in the range 400 to 500°C, followed by a fast cool. This standardizing treatment produces the glow curve normally observed, which is illustrated in Figure 1; the observed peak temperatures will vary depending on heating rate[35], hence the peaks are usually numbered as in Figure 1 to allow simple differentiation.

Additional pre-irradiation annealing treatments can alter this glow curve[94]. Annealing at 80°C for 24 h, for example, eliminates the low-temperature peaks 1, 2, and 3; annealing at 175°C for times over 3 to 4 h reduces peaks 4 and 5 to almost zero while enhancing peaks 2 and 3. Certain optical treatments can also alter the relationships between the various TL peaks[12,70].

The principal effect of thermal and optical treatments in an ionic solid is to alter the lattice defect equilibrium, including the concentration and arrangement of cation and anion vacancies, impurities, impurity – vacancy associates, and assorted electrons and holes which may be associated with such defects. The relationship between these defects and the TL process is the major topic of this paper, where various interrelationships are discussed in terms of trapping and recombination processes. Since the lattice defects themselves are crucial in determining TL behavior, however, we first present a discussion of lattice defect equilibrium. In all cases, the present paper deals with phenomena at and above room temperature.

2 – LATTICE DEFECT EQUILIBRIUM

Equilibrium relationships between lattice defects have been the subject of numerous investigations[45 to 47]. Experimentally, this defect equilibrium is perhaps most easily discussed in relation to an ionic conductivity plot, since each region in such a plot relates to a specific defect present in thermal equilibrium[39,45 to 47]. For the present paper, the ionic conductivity of pure and Mg-doped

LiF is of major importance, and is given for several doping levels in Figure 2, where the conductivity may also be compared to that for LiF (TLD-100)[88]. The ionic conductivity itself indicates the concentration and mobility of lattice vacancies. In LiF and most other alkali halides, these are the cation vacancies, which predominate due to their higher mobility as well as the higher solubility of cationic impurities; influences due to anion vacancy motion may be seen at high temperatures[43,76] and in certain anion-doped samples[65]
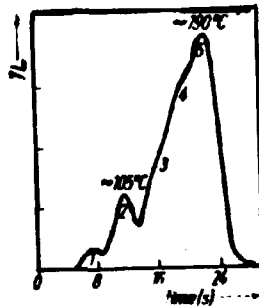

Figure 1 — Typical glow curve of TLD-100 LiF after annealing 1 h at 400°C and irradiation to 100 R.

The ionic conductivity is governed by intrinsic behavior at high temperatures and low concentrations, as indicated by region I in Figure 2. Here the conduction is governed by thermally activated vacancies, but at lower temperatures the presence of divalent cation impurities, which substitute for monovalent cations in the crystal lattice, enhances the vacancy concentration due to the need for charge neutrality in the crystal. Hence, each divalent impurity ion introduces a cation vacancy into the lattice[45 to 47] giving rise to extrinsic conduction, shown as region II in Figure 2.
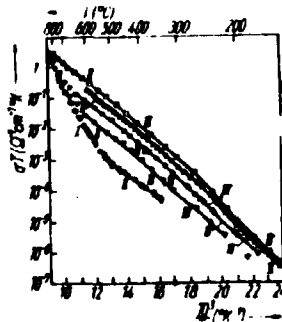

Figure 2 — Ionic conductivity curves for four purities of LiF :Mg and for LiF (TLD-100), as noted. Regions of the conductivity plot are indicated, as described in the text ▲ LiF (TLD-100); ● B 3(≈1 ppm Mg); △ R 3 (82 ppm Mg); ○ H 3 (160 ppm Mg); □ H 5 (320 ppm Mg).

At all temperatures below that of region II, the total extrinsic vacancy concentration is the same as in region II, but interactions between vacancies and impurities reduce the concentration of free cation vacancies that may respond to the applied electrical field, hence reducing the observed conductivity (regions III, IV, and V). The ionic conductivity still indicates a good deal about the equilibrium lattice defect structure in this region, however, since the free vacancy concentration in each region is governed by equilibrium reactions with each defect phase. Hence, region III is governed by interactions with Mg cation — vacancy pairs, or "dipoles"[28]; region IV with metastable precipitate particles of the type $MgF_2 . 6 LiF$, termed the Suzuki phase[2,48]; region III' with further dipole formation after the Suzuki phase can no longer form due to the low temperature[2]; region V with dipole complexes[2,28]. Models for several of these defect complexes are shown in Figure 3.
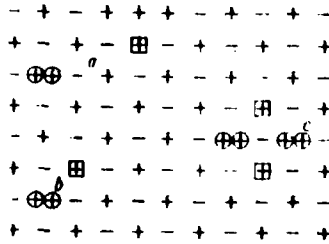
Figure 3 — Models of cationic defects in alkali halides. a — A divalent impurity ion ⊕⊖ with a dissociated extrinsic cation vacancy ⊟; b — an associated impurity-vacancy pair, called a dipole; c — a simple complex containing two dipoles: a dimer.

The formation of the Suzuki phase in Mg-doped LiF has been studied in detail by Lilley and Newkirk[48] and the results agree with similar work in other alkali halides[81 to 83,85]. The presence of the lower-temperature dipole region III' apparently depends on the system being studied: it does not appear in Ca-doped NaCl where Kirk et al.[44] show that region V transforms directly to region IV on heating. In the case of Mg-doped LiF, however, a definite region III' is seen[2,88].

Dipole formation and equilibrium may be studied using techniques such as ionic thermocurrents (ITC)[7] and dielectric loss[18], which make use of the fact that the impurity — vacancy pair acts as an electrical dipole in the crystal lattice. The decay of the dielectric loss signal with time during aging has been studied[18,30,62,84] to determine the mode of formation of dipole complexes. This work was first interpreted in terms of third-order kinetics[18]. Here, the decay in the dielectric loss signal, illustrated in Figure 4, was observed to proceed approximately in a third-order manner in the first stages (before the slight plateau), indicating that three dipoles join together to form a complex, called a trimer. After the plateau, third-order kinetics were also indicated, meaning that two dipoles join the trimer to form a pentamer, etc.
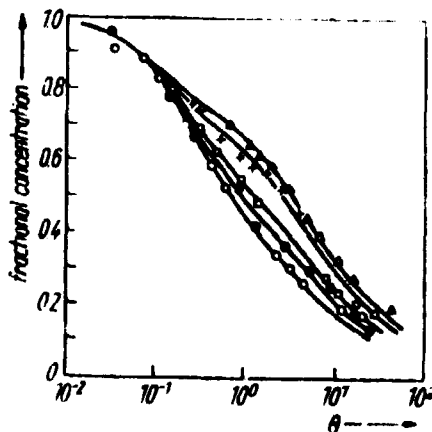

Figure 4 — Experimental data of Dryden and Shuter[29] for NaCl doped with 5×10^{-5} mole fraction of $MnCl_2$ at various temperatures (θ is the dimensionless aging time). The continuous lines are computer solutions for the dimer-trimer model (from Strutt and Lilley[77]). The data are represented by: ○ at 30°C, ● at 40°C, □ at 50°C, + at 70°C, and △ at 80°C.

This interpretation of these dipole aggregation data has been puzzling in that third-order kinetics are rare, even in interactions between gases[39]. In more recent work using ITC, Capelletti and De Benedetti[13] have shown that in Cd-doped NaCl, third-order kinetics do not completely describe the decay in the first stage. In a computer analysis which extends the analysis of Crawford[19], Strutt and Lilley[77] show that the kinetics of the overall aggregation process in Mn-doped NaCl fits best in a dimer-trimer equilibrium model, in which the trimer forms in a two-step process according to the reactions

$$D_1 + D_1 \rightleftharpoons D_2$$

and

$$D_2 + D_1 \rightarrow D_3.$$
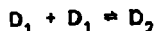
where D_1 indicates a dipole, D_2 a group of two dipoles (a dimer), and D_3 is the trimer. Curves computed by Strutt and Lilley using this model for the data in Mn-doped NaCl are shown in Figure 4, where they are seen to fit the experimental data well.

In this dimer — trimer model, the "order" of the reaction is shown to have little meaning in the first stages of decay, as it in fact changes with time. Further, this model indicates that the plateau in the curves represents dimer equilibrium, while the decay beyond the plateau at longer times is caused by trimer formation. In equilibrium, then, the dimer forms first, followed by the trimer, which seems to be the more stable defect. At lower temperatures, however, trimer formation requires a long time (in Mn-doped NaCl this requires 1 h at 129°C, 10 h at 100°C, or 100 h at 70°C), and dimer equilibrium is all that will be observed during a short-time experiment.

Several other types of impurities have the potential of changing the cation defect equilibrium, including trivalent metals such as Al and certain divalent anions[65]. Also of practical importance here is the OH ion[33,74]. Even though it is a monovalent anionic impurity, the hydroxide ion has been shown to form complexes with cation impurity — vacancy dipoles[72] and with Ti impurities[87], hence changing the normal defect equilibrium and causing a large decrease in ionic conductivity in a number of systems. In KCl, the presence of OH impurities also affects the ITC spectrum[14,73].
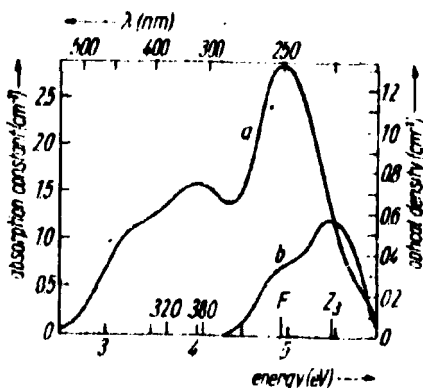

Figure 5 — Optical absorption band in LiF (TLD-100) after exposure to 3.4×10^4 R X-rays. (a) As exposed; (b) annealed after irradiation at 280°C for 15 min. Positions of absorption bands of the F and Z_3 centers and for the 310 and 380 nm bands are indicated.

Other anionic defects are important for their optical activity[32,45,71]. A single anion vacancy, for example, may trap an electron to become an F center, which is generally the predominant optical defect in alkali halides when irradiated at room temperature. Analogous centers in which holes are trapped at cation vacancies apparently do not exist, but other hole-trapped centers are important, such as V_3 centers, consisting of halogen ions which have trapped holes to form molecular halogens. V_3 centers are formed in conjunction with F centers in both pure and doped LiF[16].

When irradiated, LiF (TLD-100) and equivalent materials such as 1954-vintage LiF from Harshaw show an optical absorption spectrum with the F center[8,9,37,40,50,52] and V_3 center[50] absorptions predominating, and with somewhat smaller absorption bands at 310 and 380 nm as shown in Figure 5a. These two smaller bands have been found to be related to TL glow peaks 5 and 2, respectively[37,40,50,52]. Annealing treatments after irradiation alter this optical absorption spectrum: Annealing at 280°C for 15 min, for example, produces the spectrum shown in Figure 5b, in which the F center absorption is greatly reduced and another center is produced at 225 nm[8,9,52]. This new center has been established to be a Z_3 center, one of a series of centers involving F centers with cationic defect neighbors[38,59]. Models for the F and Z_3 centers are shown in Figure 6. All of the defects discussed here have the potential of influencing TL behavior; specific correlations are discussed in the following sections.
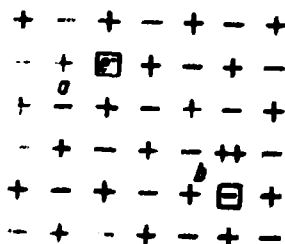
Figure 6 — Models for anionic optical defects in alkali halides. a — The F center; b — Ohkura's model of the Z_3 center.

3 — THERMOLUMINESCENT TRAPPING CENTERS

In the simple models for the TL process, each TL peak corresponds to the release of an electron or hole from a particular trapping level. In the simplest case, higher-temperature peaks would correspond to traps lying deeper within the band gap and electrons in these deeper traps require more thermal energy for release[12]. Each of these trapping levels will correspond to a defect in the crystal lattice, and a number of attempts have been made to identify specific traps responsible for specific peaks.

The decrease in the intensity of peak 2, which occurs during pre-irradiation annealing, was originally correlated with the reduction in the concentration of Mg vacancy dipoles by Grant and Cameron[36] using dielectric loss measurements. In this work, the dipole concentration was measured as a function of time in LiF containing about 100 ppm of Mg during aging at 67°C; the dipole concentration was found to be directly proportional to the height of peak 2, leading to the suggestion that these dipoles are the traps responsible for peak 2. Dryden and Shuter[29] have repeated these experiments and find a direct proportionality between dipole concentration and the dielectric loss signal in LiF only after annealing at 70°C, as shown in Figure 7a. At other temperatures there is considerable variation between dipole content and peak 2 intensity, as shown for 129°C aging in Figure 7b. In all cases, however, some relationship is evident between the dielectric loss signal and the peak 2 intensity during the initial part of the decay. This indicates that Grant and Cameron's general correlation is valid, at least to some extent, even though their observed correspondence was perhaps fortuitous.

A general correlation between peak 2 and impurity – vacancy dipole concentration is also indicated by experiments in which a certain defect structure is obtained by equilibration at a given temperature, followed by a rapid cool. Watanabe[89] has investigated the intensities of peaks 2, 3, and 5 in LiF after 10 h annealings at temperatures between 60 and 360°C. The samples were air-cooled, after which they were irradiated to a standard dose and the TL measured. Resultant TL intensities are shown in Figure 8, where it may be noted that peak 2 shows a maximum after annealing at 240°C. Ionic conductivity results (Figure 2) show that the dipole is the predominant defect in equilibrium between 240 and 450°C (region III); the maximum dipole concentration would be retained after cooling to room temperature from near 240°C. This indicates a correlation between dipole concentration and peak 2. Similar results for peak 2 are also reported in recent work by Dhar et al [27].

The results in Figure 7 and 8 both indicate a similarity in the behavior of peaks 2 and 3. Similar optical behavior is also observed for these two peaks[37,40], leading to the conclusion that the trapping centers responsible for these peaks are related to one another.
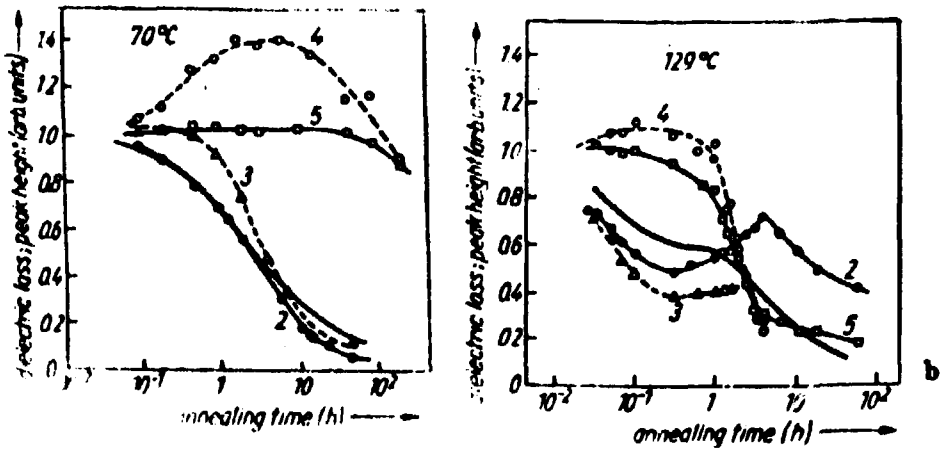

Figure 7 — The intensity of the dielectric absorption (heavy curves) and heights of peaks 2 (●), 3 (△), 4 (○), and 5 (□) in TLD-100. a) 70°C and b) 129°C. All measurements are plotted relative to the measurements at t=0, that is, immediately after a quench from 400°C.

The data of Figure 8 indicate that at low temperatures, where dipole complexes would be in equilibrium (i.e. region V of the conductivity), peak 5 grows at the expense of peaks 2 and 3, with the maximum effect seen at the lowest temperatures studied (60 and 80°C). With the 10 h annealing used in the study of Figure 8, this would seem to indicate that a simple dipole complex is related to peak 5 in this material.
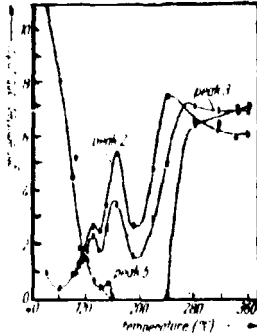

Figure 8 — TL versus pre-annealing temperature for 10 h annealing time

Further evidence for this comes from recent variable cooling rate studies[27]. If a sample is cooled rapidly from a temperature in the dipole equilibrium region (240°C and above) in LiF (TLD-100), the majority defect at room temperature will be the dipole, as noted earlier. Slower cooling will allow dipole complex formation, and based on the above, should then give a higher peak 5 intensity. This is, in fact, the case, as seen in Figure 9. The slower cooling rate maximizes the peak 5 intensity only for cooling rates above 300°C since the combination of times and temperatures during cooling allows low-order dipole complexes to form. Much slower cooling allows more time for higher-order complexes to form, and causes a large decrease in the peak 5 intensity, as is also seen in Figure 9. The coalescence of dipoles into dipole complexes during cooling from temperatures above 240°C, giving rise to increased peak 5 intensity, is also seen in Figure 8. These studies indicate that peak 5 is related to the first dipole complex to form, that is, the dimer.
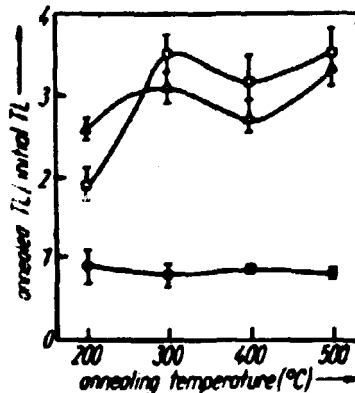

Figure 9 — Ratio of TL peak heights for peak 5 in LiF (TLD-100) after annealing at temperatures shown and cooled as noted, compared to initial TL intensity in the same specimens after a standardizing treatment. Cooling rates; △ quenched, 15 deg/s; □ air-cooled, 50 deg/min; ● furnace-cooled, 2 deg/min.

The dielectric absorption data in LiF also may be interpreted in terms of Strutt and Lilley's dimer — trimer model[77] discussed in the previous section. While most of the direct evidence for this dimer -- trimer equilibrium model refers to NaCl, evidence does exist for its application in LiF; Grant and Cameron[36], for example, observed kinetics between second and third order in his work in Mg-doped LiF. Utilizing the dimer — trimer model along with Dryden and Shuter's results shown in Figure 7[29], it may be noted that peaks 4 and 5 attain increased intensities during the first stages of aging, during which dimers would be forming, but decrease rapidly when trimer equilibrium would be established at long times. In conjunction with the data in Figure 8 and 9, this further enforces the relationship between dimers and peak 5. The point must be made, however, that the relationship is not a direct one (as is also the case for the relationship between peak 2 and dipoles), and that other factors must be considered in identifying the trapping defects exactly.

Dryden and Shuter[29] measured the TL intensities of peaks 2 to 5 during pre-irradiation aging at temperatures between 70 and 150°C for times up to 100 h, observing a large decrease in the intensities of peaks 4 and 5 at long times at the higher annealing temperatures. Mason and Linsley[51] have carried out similar long-time annealing treatments, observing a decrease in peaks 2, 3, and 5 with time for annealing up to 50 h at 100°C. The same treatment increases the intensity of a higher-temperature TL peak (at 300°C), which may indicate that this higher-temperature peak could be related to a higher-order complex whose formation is favored by this heat treatment. This increase with time of the 300°C peak was also observed on aging at 150°C, where it was further noted that peak 2 shows an initial increase in intensity followed by a gradual decrease. This may correlate with the increase in peak 2 intensity observed in Figure 8 for annealing near 160°C, and could be associated with the "freezing in" of the Suzuki phase precipitations process (Figure 2, region IV)

Other high-temperature TL peaks have been observed in LiF (TLD-100)[8,9,58,78] and in other thermoluminescent phosphors. Such deep traps generally do not affect TL induced by X-irradiation, but electrons in such traps can be transferred to other shallower traps by UV irradiation. This provides a technique for the study of such traps, as well as a mechanism for use in UV dosimetry.

Optical studies are of assistance in further determining identities of specific traps, in that relationships have been established between the optical absorption peaks at 310 and 380 nm and the TL peaks 5 and 2[8,9,37,40,50,52], as noted earlier with respect to Figure 5. In particular, peak 5 is correlated with the rapidly (optical) bleaching part of the 310 nm absorption, while peak 4 is thought to correlate with the slowly bleaching part of the same band. TL glow peaks 2 to 5, along with most of the TL glow peaks observed at higher and lower temperatures, have been established as being due to electron trapping centers, as also are their associated absorption bands[52].

The overall efficiency of the luminescence process in LiF is generally observed to be low compared with the number of electrons liberated by irradiation[12]; if the traps for peaks 2 and 5 were dipoles and dimers, for example, the efficiency would also be quite low compared to the number of these defects present. An additional problem inherent in the identification of dipoles and dimers as the TL traps comes from the low probability that such defects, which are neutral in the crystal lattice, could indeed trap electrons. The proximity of the optical absorption bands related with these TL traps to the F band may indicate that the actual traps are more like modified F centers, such as an anion vacancy near a dipole or a dimer. This general idea was suggested earlier by Mayhugh et al.[16,51] on the basis of optical correlations. Since models of this type would give a general relationship (but not an exact one) between the TL peak intensities and the dipole and dimer concentrations, they fit in well with the quenching and decay results discussed earlier.

Another interesting question regards the difference between peak 4 and peak 5 traps, both of which contribute to optical absorption at 310 nm. Using the above models, the apparent differences between the peak 4 and peak 5 traps could be due to two different arrangements of the two dipoles and the anion vacancy in the trapping complex[62]. In fact, it would be expected that in equilibrium several such arrangements could be possible. Different arrangements could give rise to

similar optical absorption characteristics but different decay and thermal release characteristics, as is observed. The same is possible regarding the related peak 2 and peak 3 traps, since several arrangements of the anion vacancy, the impurity, and the cation vacancy would be possible.

Any such identification of the specific traps is difficult to prove due to the indirect nature of the evidence available. Additional experimentation, as well as theoretical calculations of trapping probabilities of dipoles, dimers, and other defects, with and without associated anion vacancies, would be useful in this regard. Calculations regarding the validity of the dimer – trimer model in interpreting the dielectric absorption aging data in LiF would also be helpful.

4 – RECOMBINATION AND LUMINESCENCE

Rossiter et al.[67,68] have done a rather extensive study of the influence of certain impurities on the TL intensity of LiF. As noted earlier, it was found that in addition to the main Mg impurities, Ti is essential in producing high TL sensitivities, as is demonstrated in Figure 10 and 11. Figure 10 shows TL outputs from samples cut from an as-grown single crystal of LiF. It is obvious that using either zone-refined or vacuum-grown LiF, samples cut from near the tip of the crystal (the part that solidifies first) show the highest TL sensitivity. Rossiter et al. show that this increase in sensitivity at the crystal tip is in proportion to the Ti concentration: Ti concentrates in the crystal tip during solidification. The amount of sensitivity increase depends on the Ti concentration, which actually shows an optimum value as may be seen in Figure 11. Beyond the maximum intensity at 7 ppm Ti, the luminescence efficiency decreases, apparently due to luminescence quenching[67,68].

Rossiter also has shown that the ultraviolet absorption band near 200 nm is related both to the Ti concentration and to the luminescence process. That is, the 200 nm absorption band is directly related to Ti content and to the luminescence output, indicating that Ti is involved in the luminescent recombination process occurring in this material.
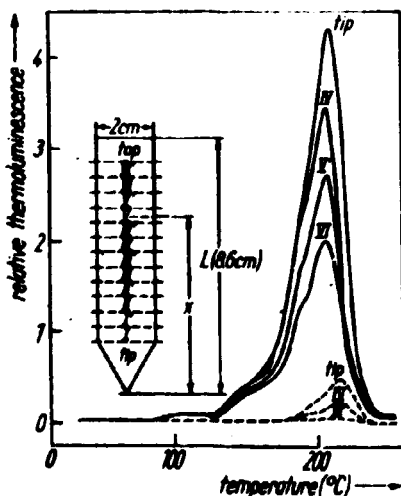

Figure 10 -- Figure on the left: method of sectioning crystals. C_0 average concentration of impurity in crystal; C_x concentration of impurity x cm from tip; k distribution coefficient of impurity. Figure on the right: glow curves from sections of crystals with Mg alone added. Dose 14 rd. — Zone-refined LiF + 80 ppm Mg; - - - vacuum-grown LiF + 80 ppm Mg.

More recent work has shown that hydroxide ion impurities are also involved in the luminescent recombination process[87,88]. In crystals containing extremely low OH impurity concentrations, the sensitivity is actually reversed from that in Figure 10: The highest sensitivity is observed in the opposite end of the crystal (last part to solidify) rather than in the tip. This is explained by the observation that OH ions are rejected from the crystal during growth and only enter the crystal lattice in the last parts to solidify.
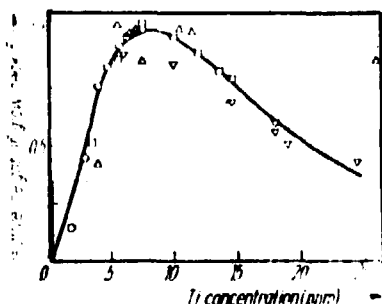

Figure 11 — Normalized height of glow peak 5 in glow curves of sections from crystals with magnesium and titanium added. Dose 10 rd. Vacuum-grown LiF + 80 ppm Mg + Ti (o 1.5 ppm, △ 3 ppm; □ 6 ppm; ▽ 15 ppm Ti)

In this latter work, the 200 nm absorption band has been related directly to the OH ion concentration, leading to the conclusion that OH ions are also involved in the recombination process. In fact, further work shows that a complex of Ti and OH ions controls the 200 nm band and the luminescent recombination. Hence, in crystals with low OH concentrations but relatively high Ti concentrations, the OH content controls the concentration of these Ti-OH complexes, as in this later work. Rossiter's crystals, on the other hand, show a high OH impurity concentration and the concentration of Ti-OH complexes is controlled by the lower Ti content.

Further evidence for the formation of Ti-OH complexes comes from the ionic conductivity work of Jain and Sootha[41]. They show that Ti ions behave like other cationic impurities and give a normal ionic conductivity plot, indicating that Ti is present in either a divalent state or in a trivalent form with a compensating cation vacancy. ESR work by Block[5] indicates that the Ti in LiF (TLD-100) and in Ti-doped LiF is either divalent or neutral; in combination with the ionic conduction results, Ti can thus be regarded as a divalent cation in LiF. This impurity can therefore form Ti cation — vacancy dipoles and higher-order complexes. Analysing their conductivity plot, however, Jain and Sootha note that for a 100-ppm-doped sample, only about 20 ppm of the Ti are in solution. They postulate that the other 80 ppm are in a precipitate form, which does not break up even at high temperatures. On the other hand, the formation of Ti-OH complexes which contain vacancies and which are closely bound together, would give exactly the same effect. Indeed, the absence of precipitated Ti in Ti-doped LiF is confirmed by recent ESR observations, in which a sharp line spectrum, presumably due to Ti, is observed in LiF containing 80 ppm Ti and in LiF (TLD-100) which contains up to 15 ppm Ti[23,75,86]; no sign of a broad line spectrum due to precipitated Ti is seen.

This evidence indicates that OH impurities are essential in the observed luminescence recombination process in LiF. Since the luminescent emission process is always the same[25,61,95], the Ti-OH complexes discussed above are probably present in all thermoluminescent LiF.

The importance of OH as an impurity in thermoluminescent LiF has not been generally recognized, although OH interactions with Mg impurities have been studied in some detail[72,74]. OH impurity effects are probably involved in such observations as that of Rossiter et al [67,68] in which a change in the 200 nm optical absorption band is observed depending on the source of the Ti introduced during crystal growth. The stability of the Ti-OH complex is noted from the observation that the ESR signal due to Ti in both Ti-doped LiF and LiF (TLD-100) is apparently unaffected by annealing and

irradiation treatments[23,75,86]. Further ESR studies, possibly including ENDOR work, could be useful in determining the environment of the Ti ions in the crystal lattice and give more information on the complex and its role in the emission process.

5 – SUPRALINEARITY AND SENSITIZATION

Dosimetry grade LiF shows a supralinear response, in which the phosphor's TL sensitivity departs from a linear relationship between TL output and dose received; the response increases by about five times at high doses, after which it decreases again, presumably due to saturation[12]. This behavior is shown in Figure 12. The increase in sensitivity attained at high doses in retained by the sample if subject to short-time annealings at temperatures up to $310°C$[90]; it is completely removed by the standard $400°C$, 1 h annealing treatment. The amount of peak 5 supralinearity in LiF (TLD-100) also depends to some extent on the energy of the irradiation[10,12,79]; irradiation at elevated temperatures decreases the supralinearity of peak 5 while shifting the maximum sensitivity to lower dose[12,24].

Other TL peaks are also supralinear, and in general it is observed that the amount of supralinearity increases with the peak temperature[58,63,78]; to highest-temperature peaks, presumably corresponding to the deepest traps, are the most supralinear ones. This may be seen in Figure 13.
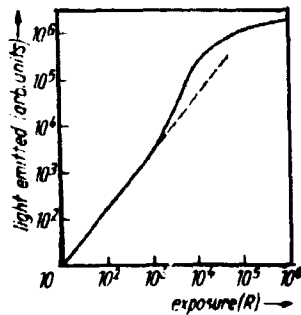

Figure 12 — Integrated thermoluminescence as a function of exposure for LiF (TLD-100). Supralinearity of the responses is shown by the departure from the dashed line.
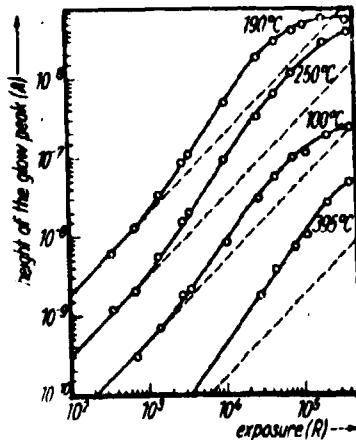

Figure 13 — Exposure versus TL peak height for different glow peaks.

Many mechanisms have been proposed to explain this radiation-induced increase in sensitivity in LiF. These mechanisms generally fit into one of two categories[95], assuming either a) an increase in the probability of charge capture at the TL traps during irradiation or b) an increase in the probability of photon emission generated by the thermal release of an electron from a TL trap during the readout.

One example of the first type of mechanism is the creation of TL traps during irradiation[11]. Another is the removal of trapping competitors, such as was proposed by Suntharalingham and co-workers[10,79,80]. In the latter mode, deep traps, which have a higher capture cross-section but are present in less numbers than the TL traps, fill up during irradiation. When these thermally stable traps become full, more electrons are available, per unit radiation dose, to fill the TL traps, providing a higher TL sensitivity at higher dose. Sunta et al.[78] have shown that this model does not hold.

The second type of mechanism would include models such as the removal of competitors to the existing luminescent centers, a model which may be closely related to Suntharalingham's model above. This type also includes models proposing the creation or activation of new luminescent centers, such as that of Claffy et al.[1,17], which proposes that recombination occurs when trapped holes from one track of ionization intersect with F centers of nearby tracks. The latter model would remain valid with the substitution of electrons for holes as the trapped species, to agree with the more recent work[95]. Other models in this category, such as those of Cameron et al.[12], which postulate the creation of new recombination centers, are unlikely since the emission (recombination) spectrum in LiF (TLD-100) always the same[26,61,95].

Zimmerman[95] has presented a quantitative approach to the supralinearity problem, comparing the relative TL sensitivities created by the two basic types of mechanisms and coming to the conclusion that a mechanism of the second type, based on an increased efficiency of the luminescence process, is responsible for the observed supralinearity. This conclusion is supported by the comparison of the growth rates of the 310 and 380 nm absorption bands, noted above to be related to peaks 2 to 5 in LiF (TLD-100). These optical absorption bands grow linearily to at least 10^5 R[1,17,68,92], whereas supralinearity becomes obvious by 10^3 R[12]. Further support for this model comes from a more recent study of the 310 nm absorption, which shows that the band magnitude is unaffected by the treatments which increase (sensitize) the TL response[8,9].

Zimmerman herself presents further supporting evidence for the relation between supralinearity and recombination in terms of her thermally stimulated electron emission (TSEE) data, and further notes the unlikelihood of the effects being induced by a change in the capture cross-section of an existing luminescent trap[95]. Furthermore, the comparison of photostimulated luminescence measurements with TL behavior allows Zimmerman to rule out an increase in the number of luminescent centers as the explanation for supralinear response. This leaves the removal of competitors to the luminescent centers, first suggested by Mayhugh et al.[51], as the most likely mechanism for supralinearity.

In LiF, a relationship between OH ion concentration and supralinearity has been reported[26,55 to 57]. In this case, the effect seems to be related to the concentration of complexes containing OH ions, Mg ions, and cation vacancies, which may be observed using infrared absorption studies[26,74]; the effect has no apparent relation with the more tightly bound Ti-OH complexes involved in luminescent recombination.

Here, the presence of Mg-OH-vacancy complexes reduces both the sensitivity and the supralinearity of thermoluminescent LiF crystals, as seen in Figure 14.

The decreased TL response observed with increasing OH ion concentration causes little or no change in the 310 nm optical absorption, indicating that the OH ions are altering the luminescent, rather than the trapping process[23,75,86].
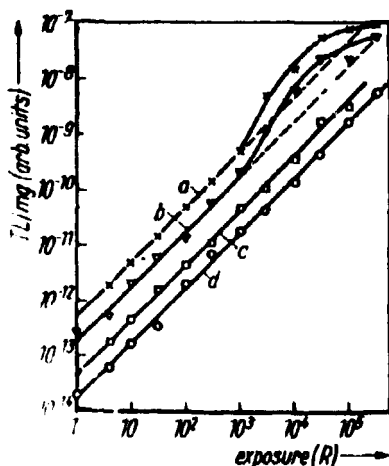
Figure 14 — Supralinearity in LiF (TLD-100) as a function of hydroxide ion addition (a) LiF (TLD-100) as received; (b) LiF (TLD-100) heated in a water vapor atmosphere; (c) LiF (TLD-100) heated in a LiOH atmosphere; (d) LiF crystal containing as-grown OH impurities.

The decrease in supralinearity with increasing OH ion concentration is consistent with a model in which Mg-OH-vacancy complexes are competitors to the normal luminescent recombination centers in the material. The competing traps could initially trap electrons during irradiation, but would not saturate at normal exposures. During read-out, electrons released from TL traps could be retrapped at these competing traps or could go to the normal recombination center, giving the normal TL output. With increasing dose, the number of electrons released from the TL traps increases, and at some point the competing traps will begin to be filled. At this point, the number of electrons combining through the normal recombination process will increase, giving rise to the observed higher sensitivity at higher dose. If the number of competing traps is increased (by increasing the OH ion concentration), it requires more electrons to saturate the competitors, until finally they never saturate, as observed in Figure 14, curves c and d.

Higher-temperature peaks, which are read out after the lower-temperature peaks, should encounter a greater amount of filling of the competing traps, giving rise to an earlier and larger relative sensitivity increase, as is observed (cf. Figure 13) Irradiation at higher temperatures will free more of the electrons from the TL traps during irradiation, filling the competitor more completely during irradiation, so that during read-out, supralinearity will appear earlier and lead to a smaller sensitivity increase than is normal, as is also observed[24] Sensitization treatments will leave the competitors partially filled, yielding the observed higher sensitivity for subsequent irradiation. This higher sensitivity level is removed by annealing at higher temperatures (400°C), probably by a radiationless recombination process.

The role of OH complexes in recombination and in supralinearity in LiF may be interrelated in some manner, as evidenced by Rossiter's observation[67,68] of a Ti-related change in supralinearity. Hydroxide ion complexes are not necessarily the only competing traps in this material, however, and several other possibilities exist, such as the isolated anion vacancy[62].

Other centers thought to have possible connections with sensitization and supralinearity have now been shown to be unrelated to this proce. . The Z_3 center, for example, and the deep traps responsible for the 280 and 370°C TL peaks may be optically destroyed, although sensitization is not affected by light[8,9,62].

6 – MODELS AND ACTIVATION ENERGIES

Thermoluminescent studies have been used for many years to derive activation parameters characteristic of the TL process. Hence, Randall and Wilkins[64] developed a simple model enabling the determination of the depth of the TL trap below the conduction band for the case of electron traps, as in LiF (TLD-100), using the kinetics of the process of electron release from the traps. These kinetics are usually reported in terms of a linear decay rate w(T), assumed to be of the form

$$w(T) = s \exp{(\frac{-E}{kT})},$$

where s is an escape frequency factor, expected to be on the order of 10^{12} s^{-1}, and E is the activation energy for escape from the trap, presumably related to the trap depth.

Numerous experimental techniques have been developed for the evaluation of the activation parameters E and s[15,34,42,54,64]. Isothermal annealing, for example, causes a decay in the peak intensity and may be analysed to determine these parameters[12,64]. Peak position and half-width, intrinsically easier to measure, have been the basis of numerous techniques[15,42]. The "initial rise" method of Garlick and Gibson[34] is often considered to be the most satisfactory experimental method for determining activation parameters, as it is applicable to a wide range of kinetic conditions[6,69] and deals only with the initial portion of a glow curve, which is presumably unaffected by the specific details of the luminescent process.

Recent theoretical work has pointed out several possible flaws in conventional activation energy determinations. In fitting glow curves with generalized kinetic equations, Saunders[69], Braunlich and Kelly[6], and Land[66] have demonstrated that glow curve shapes depend on parameters such as the ratio of re-trapping to recombination rates, the number of thermally activated traps, the number of deep traps and trap occupancy, as well as such experimental parameters as initial temperature and heating rate. Since these parameters are generally unavailable from glow curves alone, the determination of activation parameters from glow peaks may be subject to question.

It is also the case that in LiF (TLD-100), the lattice defect equilibrium and hence the trap concentrations are relatively well understood and are therefore controllable, as noted earlier. Supralinearity studies have shown that it is unlikely that deep traps and re-trapping are significant in determining the TL output of LiF (TLD-100). Hence, one should be able to test the validity of various methods of activation energy determination in this material, at least on a relative basis, and perhaps also obtain some useful information on the validity of such activation energy determinations in general.

With this in mind, a set of activation parameter determinations in LiF (TLD-100) has been compiled and is presented in Table I. As may be noted, a relatively wide variation in both peak temperatures and activation parameters is observed for the various peaks reported. The variation in reported peak temperature is understandable since peak position varies with heating rate[35], which in turn depends on thermal contact between the heater pan and the crystal[91,96]. The observed variation in activation parameters is considerable, and appears to be related to the method used: The peak shape determinations[54,91,96] not only show relatively high values of the activation energy, but also give extremely high values of the frequency factor. The initial rise values[53,91,96] are somewhat lower, but only the isothermal decay results seem generally consistent with one another.

The peak shape activation parameters are the most open to the criticisms, as mentioned earlier[6,66,69,91,96]. Here the shape of the glow peak and its maximum temperature are of utmost importance, but it is these parameters which show the greatest sensitivity to trap population, etc. Using peak shape analyses, peak 5 in LiF shows high values of E and s due to an abnormal shape: It is too narrow compared with the other peaks, and to obtain an activation

Tabela I

Activation Energies and Frequency Factors for Certain TL Peaks in LiF (TLD-100)

reference	peak	peak temperature (°C)	heating rate	method of analysis	activation energy	lg frequency factor
Zimmerman et al.[94]	4	—	—	isothermal	1.19 ± 0.05	11 to 12
	5	—	—	decay	1.25 ± 0.06	11 to 12
	6	—	—		—	22
Jackson and Harris[37]	2	115	—	isothermal	0.84 ± 0.05	8 to 10
	3	160	—	decay	0.89 ± 0.09	8 to 10
	4	195	—		1.20 ± 0.04	11 to 12
	5	210	—		1.27 ± 0.09	11 to 12
Miller and Bube[53]	2	86	linear	initial	1.07	—
	5	177	13 deg/min	rise	1.59	—
	8	242			1.98	—
Moran et al.[54]	2	102	linear	peak	1.47	18
	3	137	35 deg/min	shape	1.77	21
	5	183			2.20	23
Ziniker et al.[96]	2	97	quadratic	Kelly-Laubitz	1.10	13
	3	137	1.3×10^{-6} deg/s	(peak-shape)	1.21	13
	5	197			1.97	20
	8	265			1.96	17
Blak[3,4]	4	198	linear	computer fit	1.05	10
	5	234	2.3 deg/s	(Randall-Wilkins)	1.29	11

energy value close to that of Miller and Bube's initial rise results[53], the peak would have to be made arbitrarily several degrees wider in temperature (and even more so to match the isothermal decay results)[91,96]. This problem has been further discussed by Moran and Podgorsak[54], who show that their results can be made to agree well with the isothermal decay results by allowing small perturbations in the Randall-Wilkins model, including the possibility of a small temperature dependence in the activation energy.

The model of Randall and Wilkins is generally used in isothermal decay analysis, and may also be used to calculate a fit to the entire glow curve, as in the work of Blak and Watanabe[4]. Here, isothermal decay. results and both the separate glow curves of the peaks and the overall glow curve were fitted in a computer calculation to determine the best fit to peaks 4 and 5 together. The activation energy and frequency factor values determined here agree well with the earlier isothermal decay data[68]. In many ways, these results avoid the theoretical questions raised earlier; together with the quite-satisfactory fit obtained with the experimental glow curves, they indicate that the Randall-Wilkins model does in fact hold in LiF (TLD-100).

In general, activation parameters are usually determined with the ultimate objective of relating the trapping levels with other aspects of a model for luminescence in a solid. This is very difficult, and many inconsistencies are encountered in the various models which have been published based solely on such results[12,53]. Better results are obtained when model studies are carried out using activation parameter determinations in conjunction with other defect studies[50], but is is likely that a considerably better understanding of the lattice defect equilibrium will be required before a complete understanding of the luminescence phenomenon in LiF (TLD-100) is obtained.

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REFERENCES

1. ATTIX, F. H. Further consideration of the track-interaction model for thermoluminescence in LiF (TLD-100). *J. appl. Phys.*, Lancaster, Pa., 46:81-8, 1975.

2. BARSIS, E. et alii. Ionic conductivity of MgF_2-doped LiF crystals. *Proc. Br. Ceram. Soc.*, Stoke-on-Trent, Engl., 9:203-13, 1967.

3. BLAK, A. R. *Estudo das propriedades dos picos TL 4, 5 e 6 no LiF:Mg.* São Paulo, 1973. [Dissertação de mestrado].

4. _____ & WATANABE, S. Physical parameters of glow peaks 4, 5 and 6 in TLD-100 (LiF:Mg). In: NIEWIADOMSKI, T., ed. *Proceedings of the fourth international conference on luminescence dosimetry, Krakow, Poland, 27-31 August 1974.* Kraków, Institute of Nuclear Physics, 1974. v.1, p.169-96.

5. BLOCH, P. Paramagnetic resonance in LiF. In: AUXIER, J. A. et alii, eds. *Proceedings of second international conference on luminescence dosimetry . . . Gatlinburg, Tennessee, September 23-26, 1968.* Oak Ridge, Oak Ridge National Lab., [s.d.]. (CONF-680920) p.317-21.

6. BRAUNLICH, P. & KELLY, P. 2. Correlations between thermoluminescence and thermally stimulated conductivity. *Phys. Rev.*, Ithaca, N. Y., 1B:1596-603, 1970.

7. BUCCI, C. et alii. Ionic thermocurrents in dielectrics. *Phys. Rev.*, Ithaca, N. Y., 148:816-23, 1966.

8. CALDAS, L. V. E. *Termoluminescência radio e fotoestimulada do LiF:Mg.* São Paulo, 1973. [Dissertação de mestrado].

9. _____ & MAYHUGH, M. R. [To be published].

10. CAMERON, J. R. et alii. Supralinearity of thermoluminescent phosphors. In: AUXIER, J. A. et alii, eds. *Proceedings of second international conference on luminescence dosimetry . . . Gatlinburg, Tennessee, September 23-26, 1968.* Oak Ridge, Oak Ridge National Lab., [s.d.] (CONF-680920). p.332-40.

11. _____ et alii. Thermoluminescence vs. Roentgens in lithium fluoride: proposed mathematical model. In: ATTIX, F. H., ed. *Luminescence dosimetry: proceedings . . . Stanford, Ca., June 21-23, 1965.* Oak Ridge, Oak Ridge National Lab., Apr. 1967. (CONF-650637). p.47-56.

12. _____ et alii. *Thermoluminescent dosimetry.* Madison, Wisconsin Univ. Press, 1968.

13. CAPELLETTI, R. & DE BENEDETTI, E. Aggregation of divalent impurities in sodium chloride doped with cadmium. *Phys. Rev.*, Ithaca, N. Y., 165:981-5, 1968.

14. _____ & FIESCHI, R. Solubility of metal impurities in alkali halides, measured by means of ionic thermoconductivity. *Crystal Lattice Defects*, London, 1:69-81, 1969.

15. CHEN, R. On the calculation of activation energies and frequency factors from glow curves. *J. appl. Phys.*, Lancaster, Pa., 40:570-85, 1969.

16. CHRISTY, R. W. & MAYHUGH, M. R. Thermoluminescence mechanism in dosimetry LiF. *J. appl. Phys.*, Lancaster, Pa., 43:3216-7, 1972.

17. CLAFFY, E. W et alii. Thermoluminescence processes and color centers in LiF:Mg. In: AUXIER, J. A. et alii, eds. *Proceedings of second international conference on luminescence dosimetry . . . Gatlinburg, Tennessee, September 23-26, 1968.* Oak Ridge, Oak Ridge National Lab., [s.d.]. (CONF-680920). p.302-9.

18. COOK, J. S. & DRYDEN, J. S. An investigation of the aggregation of divalent cationic impurities in alkali halides by dielectric absorption. *Proc. phys. Soc.*, London, 80:479-88, 1962.

19. CRAWFORD JR, J. H. Aggregation of divalent metal impurity in alkali halide crystals. *J. Phys. Chem. Solids*, Oxford, 31:399-409, 1970.

20. CRITTENDEN, G. C. et alii. LiF dosimetry. 1. Optical absorption studies of LiF:Mg. *J. Phys. D, appl. Phys.*, London, 7:2397-409, 1974.

21. _____. _____. 2. The effects of Mg and Ti on the thermoluminescent emission spectra of LiF. *J. Phys. D, appl. Phys.*, London, 7:2410-21, 1974.

22. DANIELS, F. Early studies of thermoluminescence radiations dosimetry. In: ATTIX, F. H. *Luminescence dosimetry: proceedings . . . Stanford, Ca., June 21-23, 1965.* Oak Ridge National Lab., Apr. 1967. (CONF-650637). p.34-43.

23. DAVIES, J. J. EPR and ENDOR of titanium-doped lithium fluoride. *J. Phys. C, solid State Phys.*, London, 7:599-609, 1974.

24. DeWERD, L A & CAMERON, J. R *Effects of irradiation temperature in LiF (TLD-100).* Madison Wisc. Wisconsin Univ, Dept of Physics, July 1966. (COO-1105-118)

25. _____ & STOEBE, T. G The emission spectrum of LiF (TLD-100) at low and high exposures. *Phys. Med. Biol* , London, 17:187-92, 1972.

26. _____ & STOEBE, T. G. The influence of hydroxide impurities on thermoluminescence in lithium fluoride. In MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry* . Riso, October 11-14, 1971. Risö, Danish Atomic Energy Commission, Dec. 1971. (RISO 249) v.1, p 78-85

27. DHAR, A. et alii Effects of annealing and cooling processes on thermoluminescence of LiF (TLD-100) *Hlth Phys*, New York, 25:427-33, 1973.

28. DREYFUS, R. W. & NOWICK, A. S Ionic conductivity of doped NaCl crystals. *Phys. Rev.*, Ithaca, N. Y., 126:1367-77, 1962.

29. DRYDEN, J. S. & SHUTER, B The dependence of the thermoluminescence of LiF:Mg^{2+} crystals on the state of aggregation of the Mg^{2+} ions. *J phys. D, appl. Phys.*, London, 6:123-30, 1973.

30. _____ et alii. The hardness of alkali halide crystals containing divalent ion impurities. *Phil. Mag.*, London, 12:379-91, 1965.

31. FAIRCHILD, R. G. et alii Thermoluminescence of LiF TLD-100 dosimeter crystals. *IEEE Trans. nucl. Sci.*, New York, NS-21(6):366-72, 1974.

32. FOWLER, W. B , ed. *Physics of color centers.* New York, Academic Press, 1968.

33. FRITZ, B. et alii. Der Einflu von OH⁻- Ionen auf Absorptionsspektrum und Ionenleitfahigkeit von KCl-Einkristallen. *Z Phys.*, Braunschweig, 174:240-56, 1963.

34. GARLICK, G. F. J. & GIBSON, A. F. The electron trap mechanism of luminescence in sulphide and silicate phosphors. *Proc. phys. Soc.*, London, 60:574-90, 1948.

35. GORBICS, S. G. et alii. Thermal quenching of luminescence in six thermoluminescent dosimetry phosphors. 2. Quenching of Thermoluminescence. *Int. J. appl. Radiat. Isotopes*, New York, 20:843-52, 1969.

36. GRANT JR, R. M. & CAMERON, J. R. Effects of pre-irradiation annealing on the thermoluminescence and dielectric loss of LiF:Mg. *J. appl Phys.*, Lancaster, Pa., 37:3791-5, 1966.

37. HARRIS, A M. & JACKSON, J. H. Low temperature annealing behaviour of TLD lithium fluoride. *J. Phys. D, appl. Phys.*, London, Ser. 2, 2:1667-73, 1969.

38. HARTEL, H. & LUTZ, F. Zur Bildungskinetik der F-F-Folgezentren in KCl. *Z. Phys.*, Berlin, 182:111-22, 1964

39. HARTMANOVÁ, M. Impurity precipitation in alkali halide crystals. *Phisica Status solidi, A*, Berlin, 7:303-24, 1971.

40. JACKSON, J. H. & HARRIS, A. M. Wave number dependent orbital diamagnesium of electrons in metals *Phys. Lett. A.*, Amsterdam, 29:432-3, 1969.

41. JAIN, S. C. & SOOTHA, G. D Electrical and optical properties of titanium-doped lithium fluoride crystals. *Physica Status solidi*, Berlin, 22:505-16, 1967.

42. KELLY, P. J. & LAUBITZ, M. J. On the analysis of glow curves. *Can. J. Phys.*, Ottawa, 45:311-21, 1967.

43. KIRK, D. L. & PRATT, P. L. Ionic conductivity in pure and manganese-doped crystals of NaCl. *Proc. Br. Ceram. Soc.*, Stoke-on-Trent, Engl., 9:215-32, 1967.

44. _____ et alii. Ionic conductivity, ionic thermocurrents, dielectric absorption and internal friction in impure NaCl. *Proc. Br. Ceram. Soc.*, Stoke-on-Trent, Engl., 19:105-34, 1971.

45. KROGER, F. A. *Chemistry of impurity crystals.* Amsterdam, North-Holland. 1964.

46. LIDIARD, A. B. Ionic conductivity. In: FLÜGGE, S., hrsg. *Handbuch der Physik.* Berlin, Springer, 1957. Bd.20, S.246-349.

47. _____. Reaction among point defects in alkali halides. *J. appl. Phys.*, Lancaster, Pa., 33(suppl. to n.1):414-21, 1962.

48. LILLEY, E. & NEWKIRK, J. B. Precipitation in LiF crystals doped with MgF_2. *J. Mater. Sci.*, London, 2:567-82, 1967.

49. MASON, E. W. & LINSLEY, G. S. Properties of some deep traps in lithium fluoride. In: MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry ... Risö, October 11-14, 1971.* Risö, Danish Atomic Energy Commission, Dec. 1971. (RISÖ-249). v.1, p.164-184.

50. MAYHUGH, M. R. Color centers and the thermoluminescence mechanism in LiF. *J. appl. Phys.*, Lancaster, Pa., 41:4776-82, 1970.

51. _____ et alii. Color centers and the thermoluminescence process in LiF:Mg. In: AUXIER, J. A. et alii, eds. *Proceedings of second international conference on luminescence dosimetry ... Gatlinburg, Tennessee, September 23-26, 1968.* Oak Ridge, Oak Ridge National Lab., s.d. (CONF-680920). p.294-301.

52. _____ et alii. Thermoluminescence and color center correlations in dosimetry LiF. *J. appl. Phys.*, Lancaster, Pa., 41:2968-76, 1970.

53. MILLER, L. D. & SUBE, R. H. Luminescence, trapping, and F centers in lithium fluoride crystals. *J. appl. Phys.*, Lancaster, Pa., 41:3687-97, 1970.

54. MORAN, P. R. & PODGORSAK, E. B. *New developments in passive radiation dosimetry: radiation reduced thermally activated current.* Oak Ridge, USAEC, 1971. (COO-1105-164). p.155-60.

55. NAKAJIMA, T. Correlation of optical absorption with thermoluminescence of thermally treated LiF crystals. *J. appl. Phys.*, Lancaster, Pa., 39:4811-6, 1968.

56. _____. Effects of atmosphere and grain size on thermoluminescence sensitivity of annealed LiF crystals. *J. Phys. D, appl. Phys.*, London, 3:300-6, 1970.

57. _____. The influence of OH anion on the thermoluminescence yields of some phosphors. In: MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry ... Risö, October 11-14, 1971.* Risö, Danish Atomic Energy Commission, Dec. 1971. (RISÖ-249). v.1, p.90-104.

58. _____. On the sensitivity factor mechanism of some thermoluminescence phosphors. In: MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry ... Risö, October 11-14, 1971.* Risö, Danish Atomic Energy Commission, Dec. 1971. (RISÖ-249). v.2, p.446-79.

59. OHKURA, H. Z_2 and Z_3 color centers in KCl and KBr. *Phys. Rev.*, Ithaca, N. Y., 136A:446-51, 1964.

60. PATENT.
ESTADOS UNIDOS. U. S. Patent 3 320 180.

61. PEARSON, D. E. & CAMERON, J. R. *Simple TL detector using photo-resistor.* Oak Ridge, USAEC, 1966. (COO-1105-153).

62. PETIAU, J. Cinétique de guérison des défauts diélectriques de LiF. *J. Phys. Radium*, Paris, 24:564-6, 1963.

63. PODGORSAK, E. B. et alii. Thermoluminescent behavior of LiF (TLD-100) from 77° to 500°K. *J. appl. Phys.* Lancaster, Pa., 42:2761-7, 1971.

64. RANDALL, J. J. & WILKINS, M. H. F. Phosphorescence and electron traps. 1. The study of trap distributions. 2. The interpretation of long-period phosphorescence. *Proc. h. Soc.*, London, A184:366-407, 1945.

65. REDFERN, B. & PRATT, P. L. Ionic conductivity of doped NaCl crystals. *Proc. Br. Ceram. Soc.*, Stoke-on-Trent, Engl., 1:173-6, 1964.

66. RODINE, E. T. & LAND, P. L. Electronic defect structure of single-crystal ThO_2 by thermoluminescence. *Phys. Rev B*, Ithaca, N. Y., 4:2701-24, 1971.

67. ROSSITER, M. J. et alii. Impurities and thermoluminescence in lithium fluoride. In: MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry ... Risö, October 11-14, 1971.* Risö, Danish Atomic Energy Commission, Dec. 1971. (RISO-249). v.3, p.1002-14.

68. _____ et alii Preparation of thermoluminescent lithium fluoride. *J. Phys. D, appl. Phys.*, London, 3:1816-23, 1970.

69. SAUNDERS, I. J. The thermally stimulated luminescence and conductivity of insulators. *J. Phys. C, Solid St. Phys.*, London, Ser. 2, 2:2181-98, 1969.

70. SCHULMAN, J. H. Survey of luminescence dosimetry. In: ATTIX, F. H., ed. *Luminescence dosimetry: proceedings ... Stanford, Ca., June 21-23, 1965.* Oak Ridge, Oak Ridge National Lab., [s.d.] (CONF-650637). p.3-33.

71. _____ & COMPTON, W. D. *Color centers in solids.* New York, Pergamon, 1962.

72. STOEBE, T. G. Distribution of hydroxide ions in doped alkali halide crystals. *J. Phys. Chem. Solids,* Oxford, 31:1291-4, 1970.

73. _____. Distribution of hydroxide ions in doped KCl crystals. *J. Phys. Chem. Solids,* Oxford, 35:600-3, 1974.

74. _____. Influence of OH^- ions on infrared absorption and ionic conductivity in lithium fluoride crystals. *J. Phys. Chem. Solids,* Oxford, 28:1375-82, 1967.

75. _____ & DeWERD, L. A. [Unpublished results].

76. _____ & PRATT, P. L. Ionic conductivity and diffusivity in lithium fluoride. *Proc. Br. Ceram. Soc.*, Stoke-on-Trent, Engl., 9:181-92, 1967.

77. STRUTT, J. E. & LILLEY, E. Kinetics of clustering in MnCl-doped NaCl. In: REACTIVITY of solids. London, Chapman & Hall, 1972. p.84-93.

78. SUNTA, C. M. et alii. Effects of deep traps on supralinearity, sensitization on optical thermoluminescence in LiF TLD. In: MEJDAHL, V. *Proceedings of the third international conference on luminescence dosimetry ... Risö, October 11-14, 1971.* Risö, Danish Atomic Energy Commission, Dec. 1971. (RISÖ-249). v.1, p.140-55.

79. SUNTHARALINGHAM, N. *A comparison of TLD and film for personnel dosimetry.* Madison, Wis., Wisconsin Univ., 1967. [Thesis]

80. _____ & CAMERON, J. R. Thermoluminescent response of lithium fluoride to radia.ions with different LET. *Phys. Med. Biol.*, London, 14:397-410, 1969.

81. SUZUKI, K. X-ray studies of precipitation of metastable centers in mixed crystals NaCl-CdCl₂. *J. phys. Soc. Japan*, Tokyo, 16: 67-78, 1961.

82. _____. X-ray studies on the structure of solid solutions NaCl-CaCl₂. 2. Structures of {111} and {310}plate-zones. *J. phys. Soc. Japan*, Tokyo, 10:794-804, 1955.

83. _____. _____. 3. Influence of heat treatments on the diffuse reflexion of x-ray due to {111} and {310}plate-zones. *J. phys. Soc. Japan*, Tokyo, 13:179-86, 1958.

84. SYMMONS, H. F. & KEMP, R. C. The early stages of aggregation of Mn^{2+} in NaCl. *Br. J. appl. Phys.*, London, 17:607-13, 1966.

85. TOLMAN, K. Precipitation from solid solution of NaCl-CaCl₂. *Czech. J. Phys.*, Prague, 13:296-301, 1963.

86. VANA, N. et alii. Supralinearity in LiF. In: NIEWIADOMSKI, T., ed. *Proceedings of the fourth international conference on luminescence dosimetry, Kraków, Poland, 27-31 August 1974.* Kraków, Institute of Nuclear Ph, ics, 1974. v.1, p.123-42.

87. VORA, H. et alii. Hydroxyl ions and the 200-nm absorption band in Mg- and Ti-doped thermoluminescent LiF single crystal. *J appl. Phys.*, Lancaster, Pa., 46:71-7, 1975.

88. _____ et alii Influence of lattice defects on thermoluminescence in LiF. In: NIEWIADOMSKI, T., ed. *Proceedings of the fourth international conference on luminescene dosimetry, Kraków, Poland, 27-31 August, 1974.* Kraków, Institute of Nuclear Physics, 1974. v.1, p.143-54.

89. WATANABE, S. *Pre- and post-annealing properties of low temperature glow peaks 2 and 3 in LiF:Mg.* São Paulo, Instituto de Energia Atômica, abr. 1971. (IEA-233).

90. WILSON, C. R. et alii. *Stability of increased sensitivity of LiF as a function of temperature.* Oak Ridge, USAEC, 1966. (COO-1105-116).

91. WINTLE, A. G. *J. Mater. Sci.*, London, 9:2059, 1974.

92. ZIMMERMAN, D. W. & CAMERON, J. R. Supralinearity of thermoluminescence of LiF versus dose. In: McDOUGALL, D. J., ed. *Thermoluminescence of geological mat rials.* New York, Academic Press, 1968. (CONF-660919). p.485-91.

93. _____ & JONES, D. E. Photo- and thermoluminescence of LiF:(Mg, Ti). *Appl. Phys. Lett.*, New York, 10(3) 82-4, 1967.

94. _____ et alii. Thermal annealing effects on the thermoiuminescence of LiF. *Hlth Phys.*, New York, 12:525-31, 1966.

95. ZIMMERMAN, J. The radiation-induced increase of thermoluminescence sensitivity of the dosimetry phosphors LiF (TLD-100). *J. Phys., C, solid State Phys.*, London, 4:3277-91, 1971.

96. ZINIKER, W. M. et alii. *J. Mater. Sci.*, London, 8:407, 1973.