

Effect of deformation on the thermoluminescent properties of LiF and TLD 100 dosimeter crystals

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The response to ionizing radiation of LiF and TLD 100 dosimeter grade LiF, following various amounts of plastic deformation, has been investigated. The decrease in thermoluminescence with increasing plastic strain has been interpreted in terms of two models: (a) the thermoluminescence traps are destroyed by intersection or interaction with dislocation lines; (b) new thermoluminescence traps are created by dislocation intersections which then compete with the previously existing traps. The latter model is considered the more likely.

1. Introduction

LiF doped with Mg and Ti ions is now widely used as a practical dosimeter for measuring doses of ionizing radiation. The performance of Harshaw TLD 100 dosimeter crystals and "pure" LiF is known to depend upon the defect state of the crystals which is controlled by impurity atoms and thermal history. Experimental investigations [1–3] have demonstrated the importance of Mg²⁺-vacancy pairs and clusters, acting as traps, on the resulting thermoluminescence glow curves. Similarly, the importance of Ti ions in the recombination process has been indicated by several authors [4–6]. The effect of line defects, however, is less well understood. Recent studies by Srinivasan and DeWerd [7] and Petralia and Gnani [8] show that plastic deformation of TLD 100 crystals strongly decreases the thermoluminescent sensitivity. In normal use, dosimeter crystals are not deformed; however, rapid cooling following annealing can cause the generation of dislocation densities equivalent to several percent plastic strain [9, 10]. Srinivasan and DeWerd [7] concluded that the thermoluminescence decreased with deformation because the traps consisting of Mg²⁺ ions and extrinsic cation vacancies were either bound to or intersected by dislocations and

thereby rendered ineffective. The purpose of our experimental study was to obtain quantitative data for the reduction in the thermoluminescent sensitivity of TLD 100 and "pure" LiF as a function of plastic strain and to obtain, by means of dielectric loss, information about the state of Mg²⁺-V pairs in the TLD 100 crystals. This information, together with that in the literature, will be used in this paper to test different models for the attenuation of thermoluminescence by plastic deformation.

2. Experimental

Harshaw pure lithium fluoride (LiF 67) and Harshaw TLD 100 crystals, approximately 3 × 5 × 1 mm³ in size, were used throughout the current work. The experimental procedure was the same for both sets, but each was treated separately. It was standard practice to normalize all the crystals of a given batch with respect to one another prior to beginning the experiments, since individual crystal thermoluminescence sensitivities could vary by as much as ± 15%.

Batches consisting of about 24 crystals, each contained in a large pyrex tube, were annealed in air at 400° C for 60 min and cooled to room temperature at ~ 25° C min⁻¹ in still air. To prevent any possible room-temperature ageing of defects

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related to Mg^{2+} ion-cation vacancy pairs, either before or after deformation, the crystals were kept at liquid nitrogen temperature in the intervening periods. Four crystals in each batch received no deformation and were used as reference crystals for comparison.

Crystals were deformed in compression at room temperature across their large faces at a constant strain-rate of 0.05 mm min^{-1} on an Instron machine using a self-levelling compression head. At least three crystals in each batch received the same deformation. When all crystals had received their allotted deformations, the batch as a whole was allowed to reach ambient from liquid nitrogen temperature, and then immediately irradiated to 400 rad using a ^{60}Co γ source. The crystals were then again stored at liquid nitrogen temperature until required for thermoluminescence measurement. The crystals were read out at a heating rate of about $90^\circ \text{ C min}^{-1}$ and the resulting glow curves were analysed in terms of the heights of peak II and peak V. The overall error in thermoluminescence measurements was estimated to be $\pm 5\%$.

A further investigation of TLD 100 crystals was carried out using the dielectric loss technique to study the Mg^{2+} V pairs. These measurements were performed at room temperature on larger ($10 \times 10 \times 1 \text{ mm}^3$) TLD 100 crystals over the frequency range 10 to 1000 Hz, using a General Radio 1621 system. Crystals were annealed and cooled as previously described and measurements were made

both before and after 8% plastic strain. The loss peaks, extracted from the loss spectra, had ideal Debye profiles thus indicating that nearest-neighbour associated pairs dominated over next-nearest pairs. The standard analysis [11] was used to calculate Mg^{2+} V pair concentrations. From reproducibility studies this technique yielded results which had an error of $\pm 5\%$.

3. Results

The glow curve profile of an undeformed crystal of TLD 100 is compared in Fig. 1 with those of crystals which have received various plastic strains. As can be clearly seen, the general effect of deformation is to suppress the thermoluminescence response to a degree dependent on plastic strain. The high temperature peaks, IV and V, are affected the most and the low temperature peaks, II and III, the least. For example, peak V is reduced in intensity by $\sim 45\%$ after approximately 14% strain peak II is only reduced by 23% for the same strain.

Quantitative data on the reduction of the intensities of peaks II and V are presented together in a normalized form plotted against strain % in Fig. 2. (For the undeformed crystals the ratio of peak V to peak II intensity was 3.9 : 1.) These results show an apparently linear decrease in peak heights with increasing plastic strain.

The comparable results for deformed pure lithium fluoride are shown in Fig. 3 and 4 where, in the undeformed state, the ratio of the height of

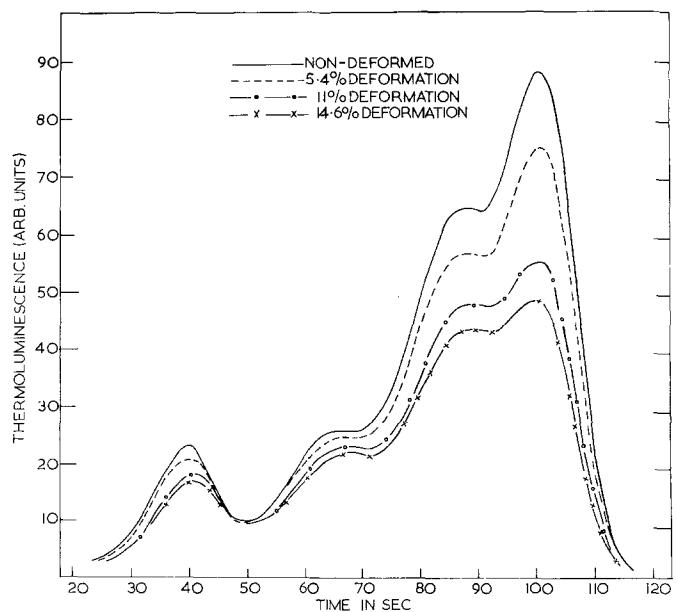


Figure 1 TLD 100 glow curve showing peaks II, III, IV and V for different amounts of plastic deformation.

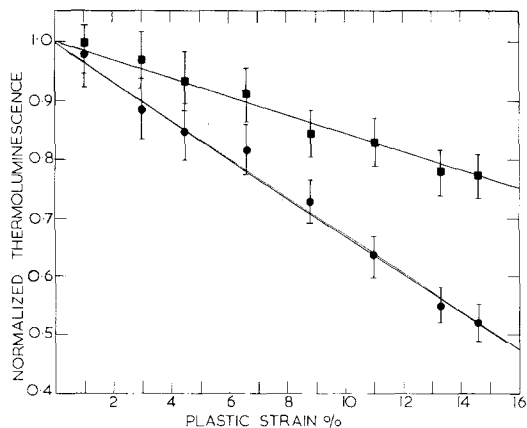


Figure 2 Normalized peak heights of peak II (■) and peak V (●) versus strain for TLD 100 crystals.

peak 2 to peak 1 is 4.1 : 1. The “pure” LiF behaves in a similar manner to the dosimetric material in that the intensities of the glow peaks all decrease in a linear fashion with strain and the high temperature peak is the most strongly attenuated (Fig. 4). The position of peak 2, however, shifts towards lower temperatures [12] (Fig. 3) whereas no such peak movement was observed for TLD 100. Generally the thermoluminescence response of pure lithium fluoride is more sensitive to deformation than that of TLD 100. If either TLD 100 or pure lithium fluoride are annealed for 1 h at 400° C following deformation, and cooled to room temperature as described previously, the

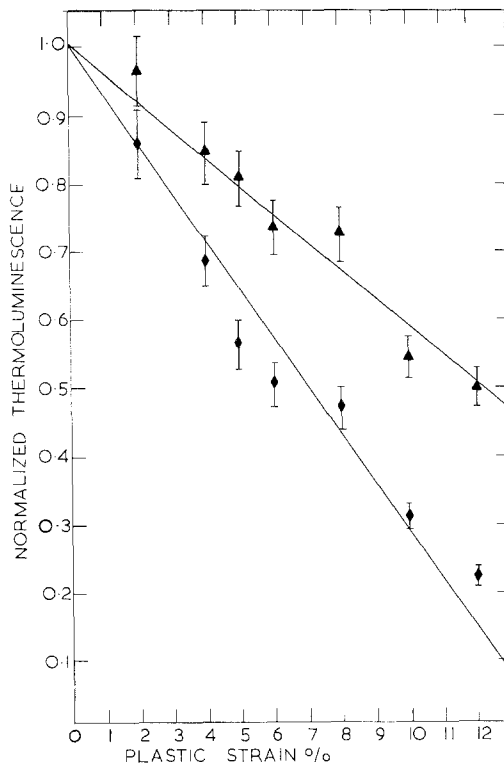


Figure 4 Normalized peak heights of peak 1 (▲) and peak 2 (◆) versus strain for Harshaw LiF.

original glow curve profile and peak intensities can be restored. This was found to be true irrespective of the plastic strain applied. Thus, the attenuating effects of plastic deformation are totally reversible for all peaks in both materials.

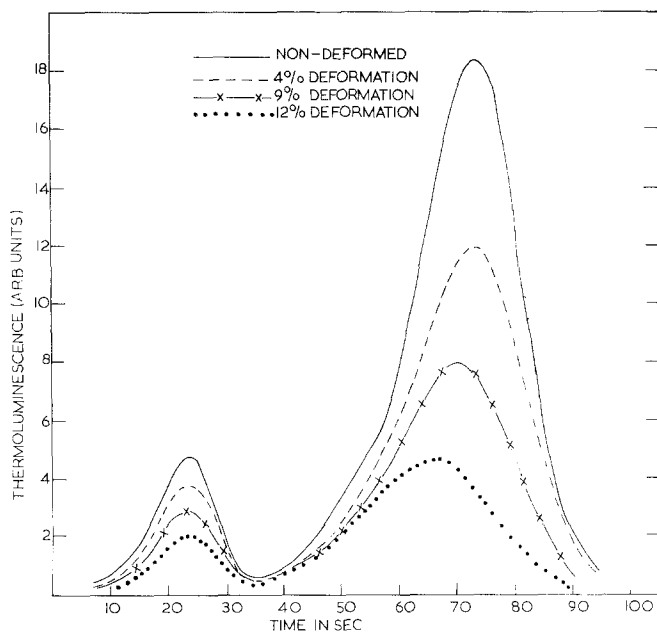


Figure 3 Harshaw LiF glow curve, showing peaks 1 and 2 for different amounts of plastic deformation.

One final result of importance is that the dielectric loss measurements, described in the experimental section, revealed that the concentration of associated pairs was the same, within experimental error ($\pm 5\%$), both before and after deformation to 8% plastic strain. Such deformations would therefore, appear to have no influence on the Mg^{2+}V associated pair concentration.

4. Models for the attenuation of thermoluminescence by deformation

It is assumed in the following that the decrease in peaks II and V in TLD 100 and in peaks 1 and 2 in LiF with increasing plastic strain is due to changes in the trapping mechanism. On this assumption, deformation could give rise to two types of interfering phenomena, namely the destruction of traps or the creation of new traps which compete with the existing ones.

4.1. Destruction of traps

If it is accepted that the defect trap for peak V is the trimer [2, 13] and the corresponding defect trap for peak II is the Mg^{2+}V associated pair [1], then the present results imply that the number of these traps, or their effectiveness as trapping centres, are reduced by deformation. Srinivasan and DeWerd [7] have proposed a model whereby the trimers are either cut by moving dislocation lines or else bound to them, so losing their effectiveness as trapping centres. Consequently, peak V would decrease with deformation as observed. Peak II is similarly decreased by Mg^{2+}V pairs becoming bound to dislocation lines, again thereby losing their effectiveness as traps.

The proposed explanation can be expressed in terms of a simple mathematical model as follows. In a single crystal the shear strain is given by

$$\epsilon = \rho b \bar{x} \quad (1)$$

where b is the Burgers vector, ρ is the dislocation density (no. per unit area) and \bar{x} is the average distance moved by a dislocation during the deformation. The area swept out by the moving dislocations is

$$\rho \bar{x} v = \frac{\epsilon v}{b} \quad (2)$$

where v is the volume of the crystal. Let us define an interaction distance, d , such that the Mg^{2+} defect-related traps lying within this distance of a

moving dislocation become ineffective. Then the total interaction volume swept out, per unit volume, is $2\sqrt{\epsilon_n} d/b$, where ϵ_n is the strain in the [100] compression direction. For a specific defect trap whose concentration is N per unit volume, the number of traps affected per unit volume is $N 2\sqrt{2\epsilon_n} d/b$ and the number of unaffected traps N' , per unit volume, is therefore given by

$$N' = \left(1 - \frac{2\sqrt{2\epsilon_n} d}{b}\right) N. \quad (3)$$

For thermoluminescence, if it can be assumed that trapping on a specific Mg^{2+} -related defect gives rise to a specific thermoluminescence peak and that, for a given radiation exposure, the intensity of that peak is directly proportional to the concentration of that magnesium defect, then it follows that the initial thermoluminescence intensity, (I_0) and the intensity after a strain ϵ , (I_ϵ), is given by

$$I_\epsilon = \left(1 - \frac{2\sqrt{2d\epsilon_n}}{b}\right) I_0. \quad (4)$$

The model thus predicts a straight line relationship between the thermoluminescence intensity (I_ϵ) and the strain ϵ , which is indeed found experimentally (Fig. 2). The interaction distance, d , can be calculated from the slopes of the graphs in Fig. 2. The resulting values are $\sim 0.4a_0$ and $\sim 0.9a_0$ for peaks II and V respectively (where a_0 is the lattice parameter). A similar treatment for the pure lithium fluoride yields d values of $\sim 1.1a_0$ and $\sim 1.5a_0$ for peaks 1 and 2 respectively.

For the specific defect traps cited by Srinivasan and DeWerd [7] for peak II, the associated pair, and peak V, the trimer, in TLD 100 the above d values would imply that dislocations, passing or lying within $\sim 0.4a_0$ of the centre of an associated pair and $\sim 0.9a_0$ of the centre of a trimer, prevent them from functioning as electron (or hole) traps.

In the case of the pure LiF, the impurity level is of the order of a few mole ppm and it appears likely that different traps are found. These would have to interact even more strongly with dislocations than the trimers and associated pairs in TLD 100 as instanced by the higher d values.

4.2. Creation of competing traps

An alternative model may be considered by assuming that deformation does not produce any marked change in the concentration of trapping species responsible for peak II and V but rather produces additional defects which compete ef-

ficiently with these traps for the available electrons and/or holes. On the alternative model, it is this competition which leads to a reduction in the observed intensities of peaks II and V. These additional defect traps must result from either dislocation-dislocation interactions or from the interaction of dislocations with defects already present in the lattice.

The competition mechanism can best be described in terms of a trapping cross-section, σ [14]. Thus for two competing traps, A and B, with concentrations N_A and N_B and capture cross-sections σ_A and σ_B respectively, the fraction of the trapped electron population, f_A , in traps A will be

$$f_A = \frac{N_A \sigma_A}{N_A \sigma_A + N_B \sigma_B} \quad (5)$$

In order for Equation 5 to be usable, an expression is needed for the concentration of competing traps (N_B). These traps will be generated mainly via dislocation-dislocation interactions and we assume that their rate of creation with strain is proportional to the strain-generated dislocation density, thus

$$\frac{dn_c}{d\epsilon} = c\rho_f \quad (6)$$

where n_c = concentration of competing traps, c = rate constant, ϵ = strain, ρ_f = freshly created dislocation density. Using the empirical relation of Johnston and Gilman [15], $\rho_f = c'\epsilon$, where c' is a constant, and substituting into Equation 6 and integrating gives

$$n_c = k\epsilon^2 \quad (7)$$

where $k = cc'$ and is a constant. The squared power in the above relation depends upon there being direct proportionality in Equation 6. A more general relation might therefore be $n_c = k\epsilon^n$, where n is some exponent.

For peak II, Equation 5 can therefore be written with the appropriate subscripts as

$$f_{II} = \frac{N_{II}\sigma_{II}}{N_{II}\sigma_{II} + k\epsilon^n\sigma_\epsilon} \quad (8)$$

f_{II} therefore represents the fraction of the initial thermoluminescence intensity of peak II remaining after a strain ϵ , i.e. I_ϵ/I_0 . Rearranging Equation 8 gives

$$\frac{1-f_{II}}{f_{II}} = \frac{I_0 - I_\epsilon}{I_\epsilon} = \frac{k\epsilon^n\sigma_\epsilon}{N_{II}\sigma_{II}} \quad (9)$$

Since $N_{II}\sigma_{II}$ is a constant, a plot of $\ln[(I_0 - I_\epsilon)/I_\epsilon]$ versus $\ln \epsilon$ should give a straight line plot of slope n .

The plots corresponding to Equation 9 for TLD 100 and pure lithium fluoride are given in Figs. 5 and 6 respectively. For such plots, the datum points for peaks II and V, and 1 and 2, can be fitted reasonably well to straight lines over the

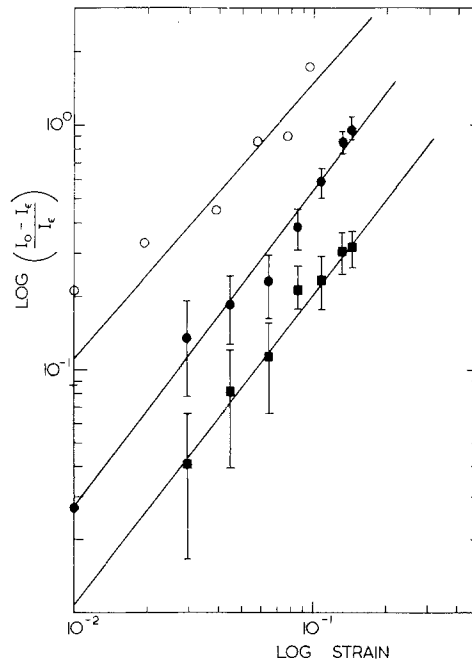


Figure 5 Plot of $\log [(I_0 - I_\epsilon)/I_\epsilon]$ versus strain for peak II (■) and peak V (●) and for peak V of Srinivasan and DeWerd (○) and TLD 100 crystals.

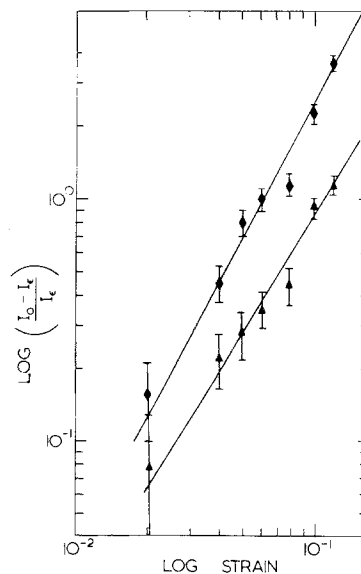


Figure 6 Plot of $\log [(I_0 - I_\epsilon)/I_\epsilon]$ versus strain for peak 1 (▲) and peak 2 (◆) of Harshaw LiF.

whole of their respective deformation ranges. The slopes of the lines for TLD 100 yield $n = 1.25$ and 1.3 for peaks II and V respectively and for pure LiF $n = 1.6$ and 1.9 for peaks 1 and 2 respectively. It should be recognized that the slopes given may be in some error owing to the large uncertainty in the points plotted at the low strains. Although the error in the original data in Figs. 2 and 4 is only $\pm 5\%$, the very large error bars in Figs. 5 and 6 arise from the $[(J_0 - I_e)/I_e]$ function. The only other data available in the literature, comparable to those presented here, are due to Srinivasan and DeWerd [7]. Their data are plotted in Fig. 5 for peak V only and can be seen to lie reasonably well on a straight line, though again the low strain points are subject to the same sort of uncertainty as just mentioned.

5. Discussion

In the last section, analytical expressions were derived for two models of thermoluminescence attenuation by deformation as a function of plastic strain, i.e. the trap destruction model and the competing trap model. Both models give reasonable agreement with the experimental results, remembering both treatments involve adjustable parameters. In the trap destruction model, the adjustable parameter is the interaction distance, d , which equals $0.4a_0$ and $0.9a_0$ for peaks II and V of TLD 100 and $1.1a_0$ and $1.5a_0$ for peaks 1 and 2 of LiF respectively. These values would be quite reasonable if the dislocations were cutting the peak II and V traps and if these traps were $Mg^{2+}V$ pairs and trimers respectively. By the same argument, the traps in Harshaw LiF would have to be larger than those in TLD 100. If, however, the dislocations became pinned by the trapping defects, rather than cutting them, it is the resulting strain field which is important, and this is not necessarily governed by the size of the defect.

In the trap competition model, the adjustable parameter is the exponent n . For the simplest case this could be assumed to be 2; however, values lower than this are found for both TLD 100 and LiF. If the newly created traps simply compete with the existing traps for electrons then it would be expected that the various peaks would be decreased by the same extent. However, in the recombination scheme proposed by Mayhugh [16], if the new traps compete for electrons with the V_3 centres and have a temperature-dependent

capture cross-section, then this could lead to a difference in the two slopes in both Figs. 2 and 4.

Alone, the analytical treatment cannot distinguish between or verify either of the two models. However, there is other evidence which should be considered. The dielectric loss measurements, made before and after 8% deformation, indicated no measurable change in the concentration of $Mg^{2+}V$ pairs. The heat-treatment used in this work led to a concentration of about 50 mole ppm of $Mg^{2+}V$ pairs, with the remaining ~ 120 mole ppm of Mg^{2+} and extrinsic vacancies presumably existing as dimers, trimers and higher order clusters. If the trimers were simply cut by dislocation lines, then the concentration of $Mg^{2+}V$ pairs should have increased. Since peak II decreased, it was proposed that the $Mg^{2+}V$ pairs became bound to the dislocation lines and thereby lost their trapping properties [7]. If this was the case, then the $Mg^{2+}V$ pairs bound to dislocation lines must have still exhibited the same Debye loss peak as in the unbound case, which seems unlikely. Moreover, a simple calculation shows that even with 10^9 dislocations/cm² there would be insufficient lattice sites on the dislocation lines to accommodate the necessary number of Mg^{2+} ions, even assuming that every site could take a Mg^{2+} ion. The dislocations would, consequently, be saturated and no linear relationship between thermoluminescent intensity and plastic strain would be expected. A recent review by Whitworth [17] suggests that some of the extrinsic cation vacancies are swept up by the moving dislocations, leaving behind the immobile divalent cation impurities. Such an effect, in which only a small fraction of the extrinsic vacancies are swept up, would not be detectable with dielectric loss for crystals as highly doped as TLD 100 (i.e. ~ 170 mole ppm Mg^{2+}). Undoubtedly $Mg^{2+}V$ clusters will be intersected by dislocations during deformation and the ions partially displaced, but these may quickly revert back to their original geometric configurations by diffusion [18]. In that case, little or no change would be expected in the concentration of $Mg^{2+}V$ pairs in TLD 100 crystals after deformation, supporting the trap competition model.

The heat-treatment at 400°C has little effect on the annealing out of the very high dislocation densities (i.e. $\sim 10^9$ dislocations/cm²) [19] yet it leads to the complete recovery of the thermoluminescence properties. Clearly these generated

dislocations are playing no significant part in the observed thermoluminescence. In the trap destruction model, both bound pairs and trimers must be released from the dislocations before repopulating the remainder of the crystal. On the other hand, in the competing trap model, we would conclude that the defects, freshly created by dislocation intersections, would simply anneal out [20].

There appear to be three or four possible types of defects which could be significant. The first, anion vacancy defects, are known to increase in concentration with increasing deformation from F-centre studies [21, 22]. Similarly, cation vacancy defects also increase in concentration, as shown by the enhanced ionic conductivity of deformed crystals at room temperature [23, 24]. Thirdly, the changes in bulk density of lithium fluoride crystals, after deformation, have been explained in terms of an increase in cation-anion vacancy pair concentration [20]. Moreover, dislocation induced vacancy clusters and dislocations themselves may act as competing trapping centres [25–27]. The increase in peak I with plastic deformation, for example, observed by Petralia and Gnani [8], could be caused by the creation of further defects, which act as traps, which are intrinsic in LiF [28].

When the thermoluminescence intensities of TLD 100, measured as a function of strain, described in this paper are compared with those of other authors, there are surprisingly large differences in the attenuation. One difference in the experimental procedures lies in the strain-rate used to deform the crystals. This information is summarized in Table I. The deformations of Petralia

TABLE I

Authors	Strain-rate (cm min^{-1})	Strain (%)	% reduction in peak V
This study	0.005	10	35
Srinivasan and DeWerd [7]	0.02	10	55
Petralia and Gnani [8]	fast	3.5	70

and Gnani [8] were performed in a vice and are therefore unspecified, but the strain-rate was probably very rapid and uneven, possibly of the order of 0.1 to 1.0 cm min^{-1} . These results do not seem to be compatible with the trap destruction model, which simply depends on strain, not strain-rate. The trap competition model, however, depends on the number of new traps created.

According to Andreev and Smirov [20] the rate of defect production is sensitive to the strain-rate, so that a four-fold increase in strain-rate almost doubles the defect concentration. This would explain the differences in results of the three studies.

Finally, if new, deep-lying traps are created through deformation, as is proposed in the trap competition model, then these traps would be expected to exert some influence on the supra-linear response of TLD 100, since this behaviour is thought to depend on such deep-lying traps [29]. In fact, a prediction of the model is that the supra-linear response should occur at higher exposures in deformed crystals because of the increased concentration of deep competing traps. Some previous results [8] do indeed indicate a delay in supralinear behaviour in deformed crystals, as would be expected.

Having considered the trap destruction model and trap competition models in some detail, both on the basis of the results presented here and those available in the literature, we conclude that the evidence indicates that the latter is the more likely model.

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