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M. T. DA CRUZ, M. R. MAYHUGH e S. WATANABE

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITARIA "ARMANDO DE SALLES OLIVEIRA"
SAO PAULO — BRASIL

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M. T. da Cruz, M. R. Mayhugh e S. Watanabe

Coordenadoria de Ciência e Tecnologia de Materiais
Instituto de Energia Atômica
São Paulo - Brasil

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M.T. da Cruz, M.R. Mayhugh[**] and S. Watanabe

ABSTRACT

The sensitization of the major glow peaks (~100 and 200°C) in fluorite correlates with the population of traps causing higher temperature glow peaks. When considered with supralinearity results, we conclude that either the sensitization results from an increase in trap-filling efficiencies, or the deeper traps are not filled during irradiation.

INTRODUCTION

Despite wide-ranging provenance and impurity content, the radiothermoluminescence (TL) glow curve in fluorite usually includes two dominant peaks above room temperature, peak[***]2 near 100°C and peak 3 near 200°C. Before mining, fluorite receives a large radiation dose ($>10^6$ rads) from natural sources and exhibits a large TL emission called the natural TL here, even when first read. In contrast, artificial phosphorus are initially TL-free. For fluorite, the natural-TL is usually eliminated by a heat treatment after which the phosphor more nearly resembles an artificial one. The predominance of peaks 2 and 3 is evident for irradiations following this treatment: our other introductory remarks also refer to fluorite thus treated.

The TL response as a function of radiation exposure is often supralinear for fluorite, and after irradiation, an intervening heat treatment may leave the substance with a sensitized response to a subsequent exposure. Sensitization and supralinearity do not necessarily go together, however. For example, peak 2 can respond supralinearly yet not exhibit sensitization, while peak 3 is not supralinear yet is sensitized. Moreover, peak 3 can be made to respond supralinearly by varying the heat treatment used to eliminate the natural-TL.

Herein we re-emphasize these facts about the supralinearity and sensitization, and note then the sensitization correlates with the creation of centers which are more stable thermally that the one under discussion. (Often "more stable thermally" is implied by the labels "high temperature" or "deep", referring respectively to the high peaking temperature of the centers' associated TL, or their equivalent larger trap depth.)

EXPERIMENTAL

Our samples, violet in color, were mined in Santa Catarina State, Brazil, and after crushing they were passed through 80 onto 200 mesh Tyler screens. Unless noted other wise, they were heated in air for 10 min at 680°C then for 95 min at 400°C to eliminate the

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[*] Presented at the IV Int. Conf. on Luminescence Dosimetry, Krakow, Poland.

[**] Present address: Department of Physics, University of Wisconsin, Madison, Wisc., U.S.A..

[***] The labels follow others' convention, except we elect Arabic numerals instead of Roman ones.

natural-TL and stabilize the subsequent response. Even so, the samples are sensitive to light and proper precautions were taken to avoid light-induced TL. The TL readings were on a Harshaw model 2000 reader using platinum alloy planchettes and modified to reach more than 500°C while still heating linearly against time, at rates of 5 or 10°C/sec. Irradiations were at room temperature, and optical bleaching was with a Bausch and Lomb SP-200 super pressure mercury lamp, without any monochromator.

RESULTS

We will conclude that a given TL peak's sensitivity depends on the pre-existing population in the traps causing the several other peaks. To demonstrate this, we have varied these pre-existing populations in several ways: the results are sub-divided according to the treatment which caused this variation.

Gamma-Ray Irradiation

Figure 1 shows a typical glow curve induced in fluorite by irradiation with ^{137}Cs to 500 R. Peaks 2 and 3 are predominant, while peak 4 near 300°C is smaller, and the several other indistinct peaks at even higher temperatures are smaller still. Usually we considered peaks 2, 3 and 4 individually while the higher temperature ones were analized collectively through their composite area.

As the exposure increases, peaks 2 and 3 exhibit increasing response, first linearly with the exposure, then supralinearly. This result is summarized in Fig. 2A where the TL induced per Roentgen (TL/R) is plotted against exposure. For this plot, linear response is occuring where TL/R is constant against exposure, and supralinear response is evident when TL/R increases with exposure. When TL/R decreases toward zero, the response is saturating. From the figure we see that peak 2 has considerably more supralinearity than does peak 3.

Fig. 2A shows the inherent sensitivity of the phosphor to different exposures. A history of high exposure may alter this inherent sensitivity, as is well known1)2). For example, an initial high exposure ($>10^3$ R) may be followed by an intervening anneal at 400°C to eliminate peaks 2, 3 and 4, but leave the higher temperature TL. Then a subsequent low exposure ($<10^3$ R) reinduces peaks 2, 3 and 4 but with sensitivities (S) different than before (S_0). The resulting increases in sensitivity to low exposure are shown in Fig. 2B for peaks 2 and 3 as a function of the previous exposure. Comparing Figs. 2A and 2 B, we see that the peak least supralinear is most sensitized, and vice versa. (Okuno and Watanabe3) have noted that this situation can be carried to the extreme: peak 3 without any supralinearity is sensitized, while a supralinear peak 2 is not.) We note also that sensitization is greater the higher the peak temperature for peaks 2, 3 and 4, a situation also noticed in dosimetry LiF.4)

Of greatest interest to us is a correlation between the increased sensitivities of peaks 2 and 3 and the area of the high temperature TL, as shown in Fig. 3. Here the increase in sensitivity is plotted against the area comprising the high temperature TL peaks which were not eliminated by the 400°C anneal. Notice that we are considering the fractional increase in sensitivity (S/S_0-1), not simply the sesitivity. In analogy with artificial phosphors, S_0 is taken as the sensitivity of the sample after removal of the natural-TL.

Annealing

The results of Fig. 3 suggest that sensitization results from the filling of the high-temperature TL-traps. To test this idea, we induced the high temperature TL by high exposure (~ 10^7 R in a shut-down reactor) and then slowly caused its destruction by annealing at 380°C. Fig. 4 shows that as the high temperature TL is destroyed, the sensitivity decreases. (Annealing alone may affect the sensitivity; hence, S_0 here is taken from a control sample which received all the treatments of the sensitized one, except the high exposure.)

After high exposure, the intervening anneal may be at a temperature low enough so that only peaks 2, 3 or 4 are removed, while the high temperature TL is unaltered. Even so, sensitivities are altered. For example, annealing at 210°C principally removes peak 4, and the sensitivity of peak 2 varies linearly with this removal. (Peak 3 is not easily observed in this experiment because at low exposure it is dominated by the overlapping tail of the larger, residual peak 4.) Okuno and Watanabe[3] have shown that the sensitivity of peak 2 is also altered by the filling of peak 3 traps. Hence, although peaks 2 and 3 have sensitivities which depend on the filling of high temperature traps, they also depend on the filling of peak 4 traps and peak 2 on the filling of peak 3 traps.

As mined, fluorite has already received a high radiation dose, and considerable high temperature TL is present, namely the natural-TL. Hence, we expect that virgin fluorite is sensitized, and annealing away the natural-TL should reduce the sensitivity in a way similar to that illustrated in Fig. 4 In fact this effect was observed, but the results are not presented here since they are redundant, and because choosing S_0 in this case is more arbitrary.

Optical Bleaching

The populations of deep traps after high exposure can also be altered by ultraviolet light. At room temperature this optical bleaching is too slow to be useful; hence we optically bleached samples at about 350°C. In particular, a sample was given high exposure (~ 10^7 R in the shut down reactor), then was exposed to intense ultraviolet light while held at 350°C. Next the sample was annealed 5 min at 400°C to eliminate any light induced peaks, and finally a test exposure (100 R) was administered to check the sensitivity. The light applied at high temperature removes the high temperature TL much faster (~ 5 min) Than annealing alone (more than 100 hrs at 400°C) or optical bleaching at room temperature (bleaching very slow ~ several days). Fig. 5 shows that varying the high temperature TL optically also causes the sensitivity to vary, again linearly with the change in area. Here the sensitivity does not appear to be returning to S_0 however.

DISCUSSION

Sensitization in fluorite can be examined by considering two experimentally established facts: 1) Supralinearity and sensitization do not go hand-in-hand; a peak exhibiting supralinearity might not be sensitized, and vice versa (cf. Fig. 2 and Okuno and Watanabe[3]). 2) A peak's sensitivity increases when higher temperature traps are occupied. In particular, the sensitivities of peaks 2 and 3 vary approximately linearly with the area of the TL remaining in the 400 - 550°C region (Figs. 3, 4, 5), although the sensitivity of peak 3 (and 2) depends also on the population of peak 4 (and 3) (our results, and Okuno and Watanabe[3]).

Filling deep traps might alter a shallow peak's response in two ways, as summarized in Fig. 6. The first possibility is illustrated on the left where during irradiation the deep traps (D) and the shallow ones (S) divide the available charge carriers, fraction δ entering shallow traps. If the deep traps fill before the shallow ones, more charge carriers will be available for the shallow traps; δ will increase and supralinearity will be obeserved since during heating more carriers will be available to produce light. This competiton in the filling process has been proposed by others[3][5]. Notice, however, that if the deep and shallow traps fill at comparable rates, δ won't change during filling, and no supralinearity need result. (More free carriers must recombine, however, or be trapped elsewhere.) In either case, annealing after irradiation empties the shallow traps, but not the deep ones, and a subsequent irradiation finds more carriers available for the shallow traps (δ increased): hence, the response may be sensitized, with or without supralinearity.

The second possibility is that δ is always constant, that is, filling efficiencies do not change. During heating, however, carriers from shallow traps may fall into deep ones, or proceed to luminescence sites, fraction γ proceeding to such sites. (The fall into the deep trap is assumed to be radiationless.) Now as the deep traps fill, supralinearity will be observed as γ increases, and sensitization will persist after annealing so long as the deep traps remain filled. (This process, a competing radiationless transition is also proposed by others[7][8].) (As an aside, notice that any change in luminescence efficiency implicitly assumes the existence of some competing radiationless, or undetected, transition because if there were no radiationless paths, all liberated charge would necessarily cause photon emission, and constant luminescence efficiency would result.)

Now if the deep traps fill during irradiation and if the sensitivity results from a competition in the luminescence process, supralinearity and sensitization must be interrelated. In particular, a peak which is not supralinear would be competing for its carriers during read-out, and since we're assuming that competitors are removed only during irradiation, the peak without supralinearity could not be sensitized. The argument can be extended to say that a peak can not be more sensitized than it is supralinear. Peak 3 conflicts with this conclusion, hence, we conclude that one of the assumptions is wrong for fluorite. (The verbal analysis presented above is merely a special case of the more complete analytical one expounded by Zimmerman.[9] In fact comparing the growth of TL/R and S/S_0 as functions of exposure reveals that these grow at rates different by a factor of 2.3 for peak 3; an observation consistent with identification of a change in filling efficiency.)

The simple two-trap models summarized in Fig. 6 are not realistic since in fluorite several traps compete with one another for the available charge carriers. This more complex situation could account for the details of fluorite's behavior. First, the simple models imply that when the deep traps are empty, the sensitivity should return to its initial value. When the deep population is increasing this is observed (Fig. 3), but for decreasing populations (Figs. 4 and 5) the sensitivity is not returning to S_0. We speculate that this discrepancy would be explained if the detailed competition were understood. Moreover, since the samples are sensitive to light, even after reduction of the natural-TL, we know that what we call S_0 does not correspond to the case of completely empty deep traps.

Changes in the relative filling of the several traps may explain why peak 3 can be supralinear in one case, and not in another. More complete removal of the natural TL reduces the sensitivity of peak 3, but increases its supralinearity, presumably because more competitors are present and they fill relatively more quickly. Peak 2 is the most supralinear of all probably because it is the most affected by the filling of 3 (and others). After sensitization 2 and 3 again compete with one another for available charge (an increased amount since the deep traps are filled); since 3 still captures most, 2 is least sensitized. (Considerably higher sensitizations can be realized for peak 2 if peak 3 traps are left occupied cf. Okuno and Watanabe, confirmed also in this work.

Returning to the main point, we conclude that either sensitization in fluorite occurs from a filling competition among the several traps, or the competing high-temperature centers are formed during the TL reading, and not during irradiation. The details of fluorite's behavior seem to be consistent with a filling competition among the several traps.

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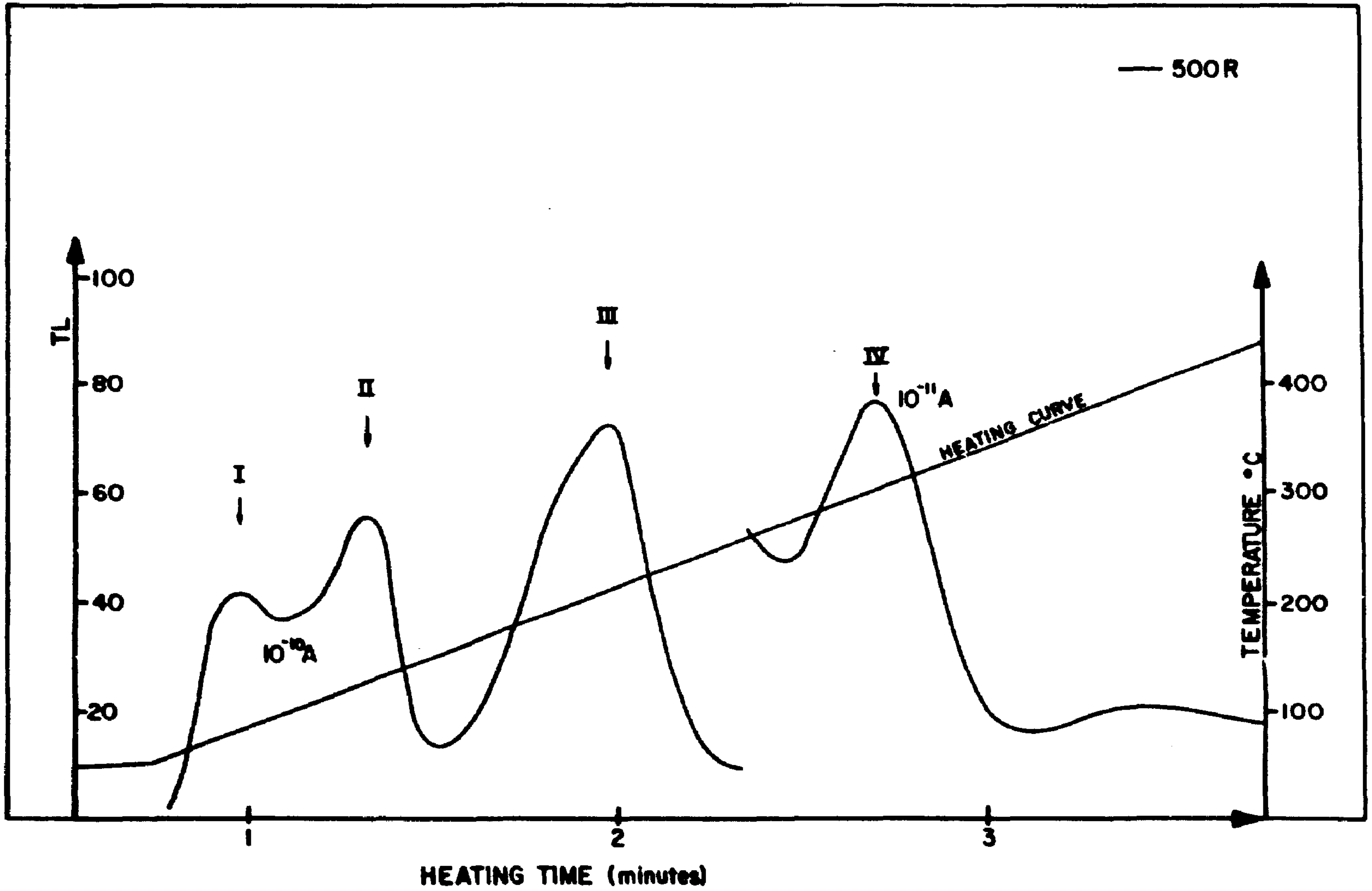

Fig. 1
HEATING TIME (minutes)
A typical glow curve from fluorite irradiated to 500R with ^{137}Cs

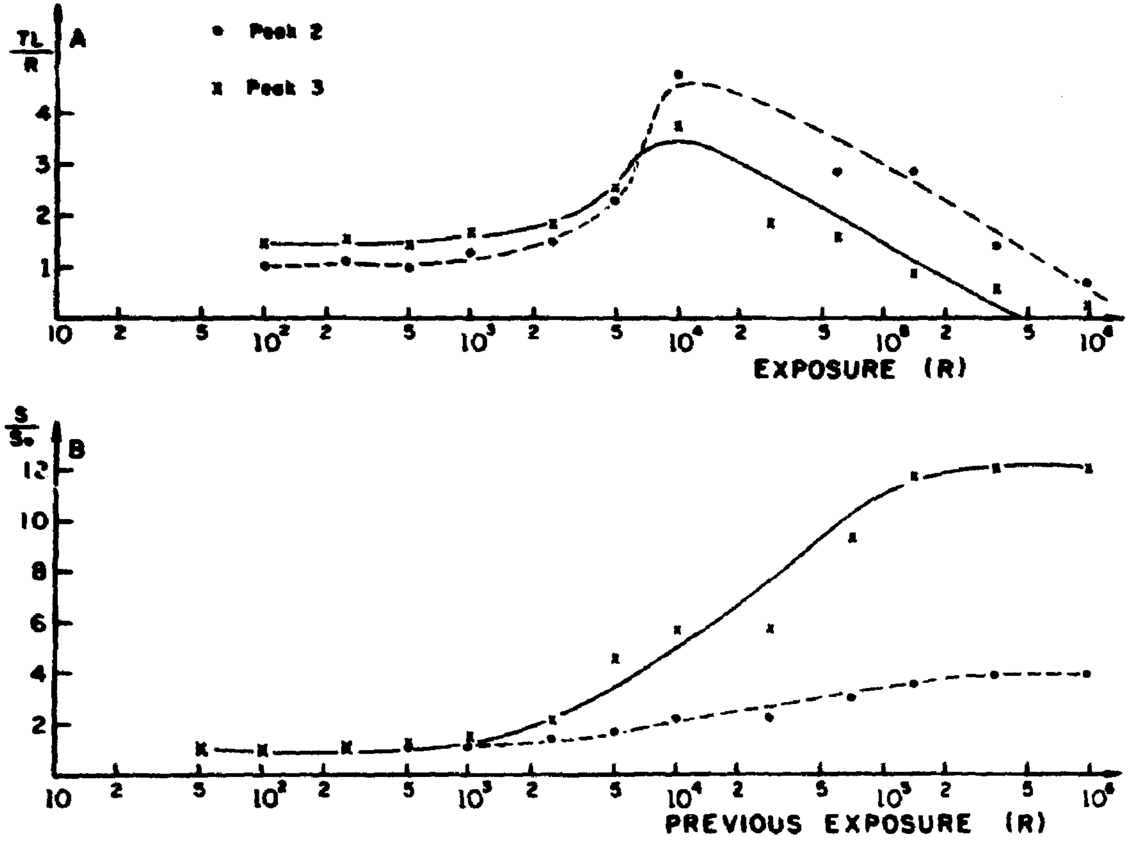

Fig. 2
PREVIOUS EXPOSURE (R)

(A) Response - The sensitivity (TL/R) as a function of exposure

(B) - Sensitization - The response to 100R (S) divided by the original response to 100R (S_0) as a function of previous high exposure. The high exposure was followed by 5min at 400°C.

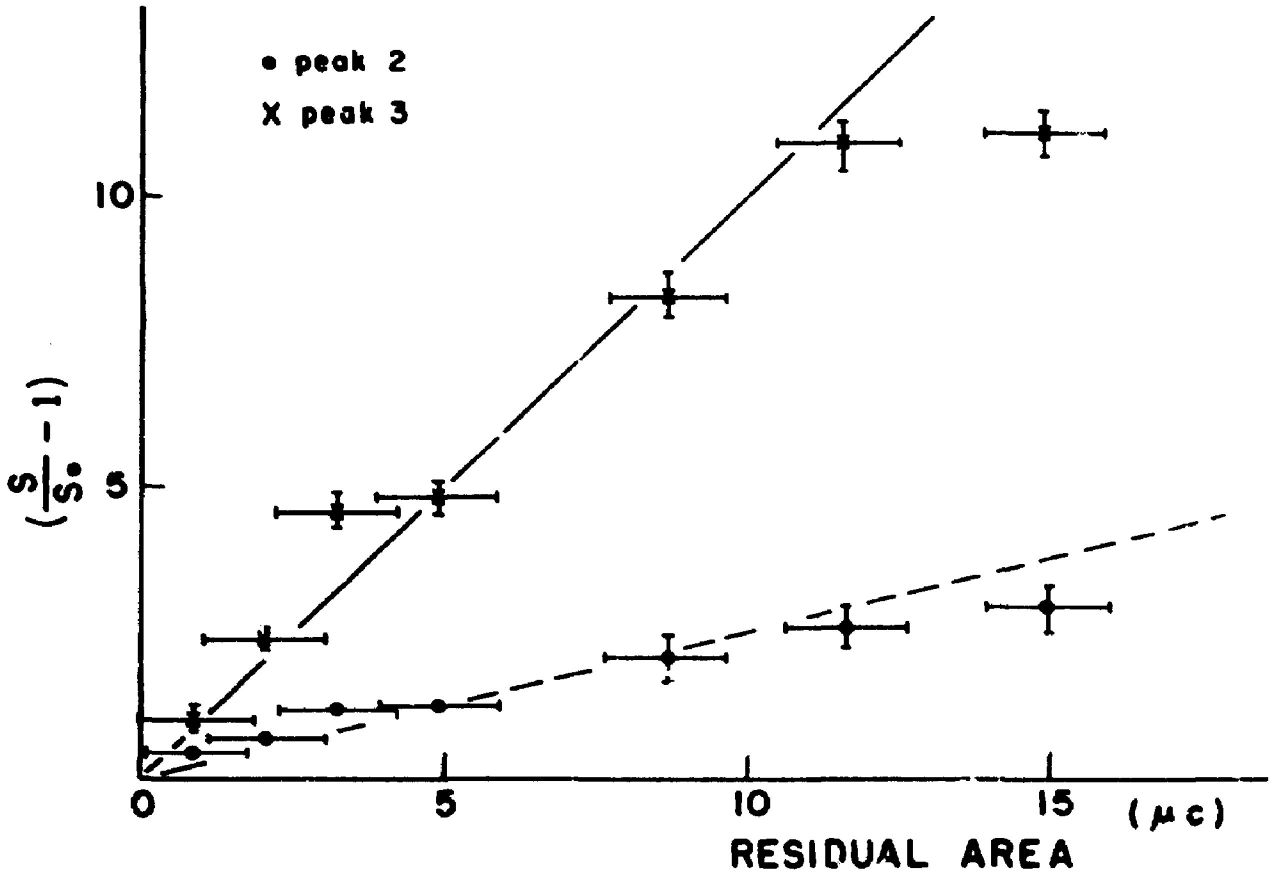

Fig 3

Residual Area (μc)

The normalized increase in sensitivity for peaks 2 and 3 as a function of the area comprising the high temperature TL. This TL was growing due to irradiation.

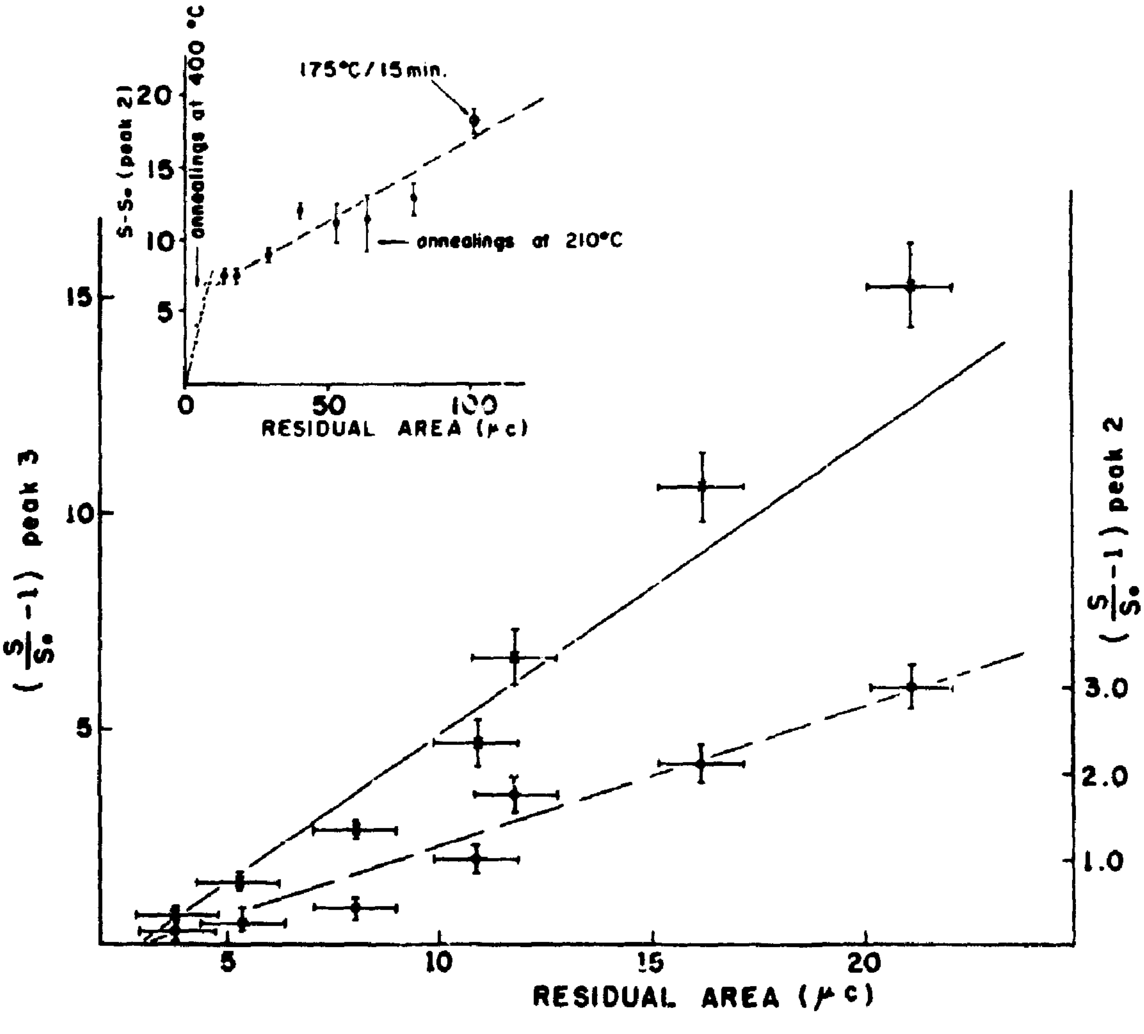

Fig. 4

Residual Area (μc)

The normalized increase in sensitivity for peaks 2 and 3 as a function of the high Temperature TL's area. This TL was falling due to annealing at 380°C.

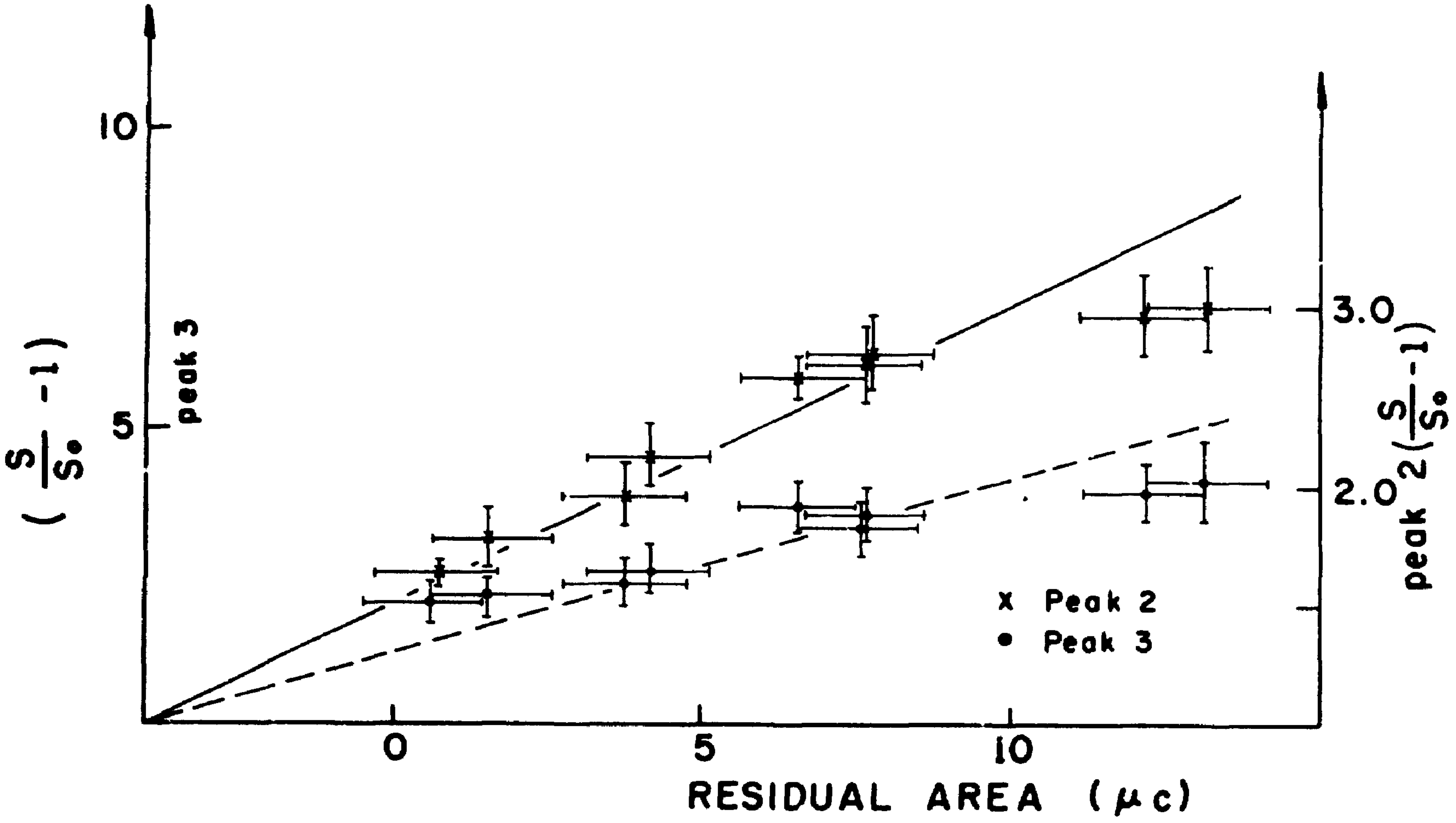

Fig. 5

Residual Area (μc)

The normalized increase in sensitivity for peaks 2 and 3 as a function of the high temperature TL's area. This TL was falling due to optical bleaching at ~350°C.

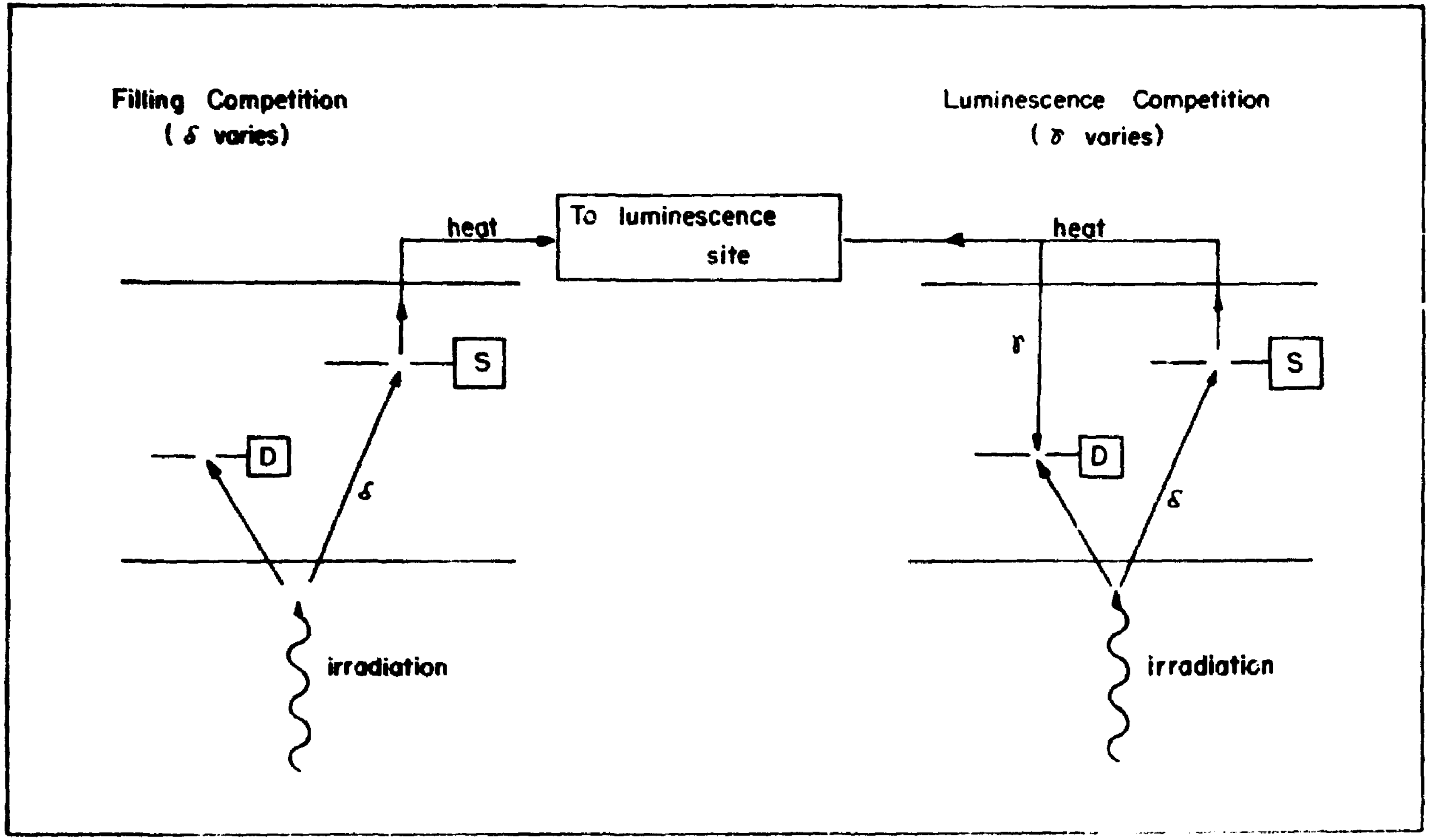

Fig. 6
Schematic models for alterations of filling efficiency and luminescence efficiency caused by filling of deep traps.

RESUMO

A sensibilização dos picos de emissão termoluminescentes (~ 100 e 200°C) da fluorita correlaciona se com a população das armadilhas responsaveis pelos picos de emissão em temperaturas mais altas Quando comparados com os resultados da supralinearidade indicam que a sensibilização resulta de um aumento na eficiencia de preenchimento das armadilhas ou que as armadilhas profundas não são preenchidas durante a irradiação gama

RESUME

La sensibilisation des pics d emission thermoluminescente (a ~ 100 et ~ 200°C) de la fluorite depend de la population des pieges responsables des pics aux plus hautes temperatures La comparasion avec les resultats de supralinearite indique que la sensibilisation resulte d une augmentation de l'efficacite de remplissage des pieges ou les pieges les plus profonds ne se remplisseent pas au cours de l irradiation gama

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