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OPTICAL STUDIES OF ELECTRON AND HOLE TRAPPING LEVELS IN QUARTZ

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OPTICAL STUDIES OF ELECTRON AND HOLE TRAPPING LEVELS IN QUARTZ*

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ABSTRACT

Illumination with monochromatic light into various color-center absorption bands of quartz at liquid nitrogen temperature (LNT) after previous X-ray irradiation at room temperature (RT) re-excites some glow peaks of the "usual" glow-curve in the region between LNT and RT. Re-excitation can also be performed for peaks above the temperature at which the crystal was x-irradiated. The effect has been investigated in detail for crystals doped with various impurities and under various conditions. The results are in agreement with the generally accepted models for the electronic processes in Quartz.

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1. INTRODUCTION

Thermoluminescence is known to be a very sensitive tool for the study of trapping centers in the solid state.

The thermoluminescence of quartz has been the subject of investigations carried out by a number of workers. Yokota[1] and Kikuchi[2] pointed out the similarities between quartz and fused silica glow-curves. These authors and Hensler[3] compared glow-curves with optical absorption for fused silica. Arnold[4] carried out the same study in crystalline quartz. Batrak[5] studied the effects on thermoluminescence of diffusion of Li^+ and Na^+ into natural single crystals. Medlin[6] attempted to determine the cause of the prominent glow-peaks in natural quartz. The present author[7] was concerned with the glow-curves as well as the spectral distribution of the glow in synthetic quartz containing aluminum impurity.

It has been noted by some of the previous authors,[4,6] that "an apparent excitation by UV, of all the glow peaks produced by X-ray irradiation, can be observed in quartz samples which were not completely thermally bleached, after previous X-ray irradiation."

It was the aim of the present work to investigate this "re-excitation" effect in detail. It is shown that the glow peaks obtained under these conditions do differ in some respects from those obtained by "usual" X-ray irradiation, and that the effect enables one to distinguish between peaks due to released electrons and those due to released holes. Furthermore it will be evident that utilizing a combination of X-ray and ultraviolet excitation is an efficient means for resolving various color centers unresolved hitherto, and in general it adds to the understanding of the thermoluminescent processes in quartz.

2. EXPERIMENTAL

The crystals used, their origin, and typical impurity content obtained by spectroscopic emission analyses are given in Table I.

Table I

Origin and Impurity Content in p.p.m. of Quartz Samples

Source	No	Al	Ge	Li	Na
Clevite Co.	33C - 4_2	105	593	56	25
Bell Tel. Co.	R-27	675	838	875	80
Sawyer Research Associates	X-21	20	4000	5	40
Bell Tel. Co.	R-537	225	0	26	80
Madagascar	Plate 117A	60	< 10	< 20	20

The crystals were X-rayed in complete darkness using a Dunlee X-ray tube (with a tungsten target) operated at 50 KVP and 15 mA. The light source was a General Electric H85 A3uv type mercury lamp. The light was passed through a Leiss single monochromator with a quartz prism. The crystal was mounted in a vacuum cryostat[8] with its window as close as possible to the exit slit of the monochromator.

The temperature of the crystal was raised linearly,[16] during the glow measurements, at a rate of 10 deg/min. Temperature readings were made with a calibrated copper-constantan thermocouple with one junction fixed near the crystal and the other one in an ice bath.

The procedure for obtaining "usual" glow curves (x glow) was as follows:

a. Sample cooled in vacuum to LNT (77°K) (or held at RT, approximately 300°K)

b. X-rayed at LNT (or at RT)

c. Crystal heated linearly and the glow curve recorded.

The light emitted by the sample was detected with a 1P28 photomultiplier. The photomultiplier current was amplified by a Keithley Model-410 micro-microammeter and recorded with a Varian Type G-14 recorder.

The procedure for obtaining re-excited glow below RT was:

a. Sample irradiated with X-rays at RT.

b. Cooled down to LNT (in vacuum) in darkness.

c. Illuminated by light of the proper wave-length.

d. Crystal heated and the glow recorded.

The procedure for re-exciting glow above RT was:

a. Sample irradiated with X-rays at RT.

b. Heat the crystal above the temperature of the peak to be re-excited.

c. Crystal cooled down to LNT (to RT in some cases).

d. Illuminated with proper wavelength.

e. Crystal heated and the glow recorded.

During all the measurements special care was taken to protect the sample from light except when it was intentionally bleached. The crystal holder dimensions in the cryostat, and hence the crystal dimensions were about 5 x 8 x 1 mm. The samples were optically polished and in a special series of measurements; it was made sure that the measured temperature was indeed the actual temperature of the crystal (within less than 0.25°).

3. RESULTS

In a set of experiments it was found that the efficiency of the re-excitation as a function of illumination time goes through a maximum and decreases with longer times. In general, a time of about 15 minutes was found to be fairly satisfactory in the present experimental conditions. This is in parallel with the results obtained by Braner and Israeli[9] in their experiments concerning alkali halides. The dependence on X-ray dose and X-ray energy seems, however, in the present case not to be as pronounced as in the case of the alkali halides.

I. Clevite (33 C-4_2) Ge-doped Quartz

Figure 1, curve (a), shows the regular glow-curve obtained for the Clevite Ge-doped crystal between LNT and 300°K after 20 minutes of X-ray irradiation at 77°K (X-glow). Figure 1, curve (b), is the optically re-excited glow for the same temperature range. In this case X-ray irradiation took place at RT for 20 minutes (instead of at LNT), followed by illumination at LNT with λ = 280 mμ for 15 minutes. Note that the 257°K peak does not appear in curve (b). This peak and only this one can be re-excited by illuminating with 440 mμ light.

Figure 2, curve (a), shows the X-glow for the Clevite Ge-doped crystal between RT and 500°K (X-ray irradiation at RT for 10 minutes). At 500°K the heating was stopped and the crystal was cooled to RT. Illumination with λ = 280 mμ for 10 minutes at RT gave the re-excited glow shown in Figure 2, curve (b). (On a three-times enhanced scale). Note that the main peaks at about 368, 395 and 460°K reappear upon excitation. One can repeat this procedure a great number of times as long as one does not heat the crystal above the last glow peak (at about 600°K). In fact as many as ten cycles of heating, recooling to RT, and illuminating again, resulted in glow of almost the same intensity as in the first cycle.

Figure 3, curve (a), shows the intensity of the re-excited glow peak at 368°K as a function of the wavelength of the illuminating light. Curve (b) on the same figure shows the X-ray induced absorption bands for comparison. One can see that while illuminating in the ~ 280 mμ band is efficient in re-exciting, the 368°K peak, illuminating in the ~ 440 mμ band is not. The variation in intensity of the source with wavelength was taken into account plotting Figure 3, curve (a).

In addition it was found that some glow peaks re-appeared in crystals that had been subjected to specific series of treatments, after they had remained in the dark at RT. Curve (a) in Figure 4 shows the result of re-heating a the Clevite crystal immediately after it has been subjected to a cycle of X-ray irradiation at RT and then heating it to ~ 500°K. As one should expect, glow is not observed during the second heating cycle as long as one does not heat the sample above ~ 500°K, for the reason that the first heating cycle has emptied all traps that could be emptied at temperatures below 500°K. After the crystal was heated to 475°K for the second time, cooled to RT and kept in the dark for 17 hours a third heating cycle produced the glow-curve shown as (b) in Fig. 4. Note that peaks now occur at 410°K and 460°K and that the peak at 368°K, which is the most intense one produced by optical re-excitation, does not occur in this case, at all.

II. Bell R-27 (Ge-doped) and Sawyer (X-21 (Ge-doped) Crystals

Essentially the same results have been found for these Ge-doped crystals. The only differences were in the relative intensities of various glow peaks. These differences have been investigated[15] in some detail, but this seems to be outside the scope of the present work.

III. Bell 537, Ge-free Quartz

Figure 5, curve (a), is the plot of the regular glow curve (on a 50-fold reduced scale) for the Bell 537 crystal between LNT and RT after X-irradiation for 10 minutes at LNT. Figure 5, curve (b), is the re-excited glow-curve for the same temperature region after illumination for 15 minutes with λ = 280 mμ. Comparing curves (a) and (b), one notices that in (b) the peak at 219°K is "missing". Figure 5, curve (c) is the re-excited glow-curve for the temperature region between LNT and RT after illumination for 15 minutes with 435 mμ light. Note that only the 219°K peak appears in this case and all the other peaks appearing in curve (b) are "missing". (Curves (b) and (c) were obtained after X-irradiation at RT for 10 minutes and proper illumination at LNT for 15 minutes.) Inspection of Fig. 5 shows that curves (b) and (c) combined, include the same glow peaks as curve (a) does, except that the intensity is higher in the latter.

Figure 6 (a) shows the relative intensity of the re-excited glow peak at 190°K as a function of the wavelength of the illuminating light. It is evident that a color center peaking below the wavelength region of our experimental set-up is the one mainly responsible for the re-excitation. The shoulder at about 280 mμ might be due to traces of Ge present in the crystal. It is of interest to note here that numerous overlapping bands are formed in the UV by X-ray irradiation. Optical absorption measurements do not resolve the various bands, and upon X-ray irradiation one gets in the absorption spectrum of this crystal the absorption bands at ~ 440 mμ, and merely a general increase of the optical density in the region 200-350 mμ.

Figure 7 shows the glow curve (X-glow) for the Bell 537 crystal for the temperature region 300-650°K.

Attempts to re-excite the glow peaks which occur above room temperature either by ultra-violet or visible light, have failed. Moreover, if the RT X-rayed crystal is heated to about 400°K, one is no longer able to re-excite with UV light even the peaks which occur below RT. However, the 219°K peak can be re-excited by 435 mμ light in a crystal that has previously been exposed to X-rays at room temperature and heated as high as 500°K.

IV. Madagascar (Plate 117A) Rose Quartz

Results are obtained in this crystal which are similar to those in the Bell 537, one difference, however, being some shifts of various glow maxima on the temperature scale. Another difference is in the low intensity of the re-excited glow as compared to the same glow in the Bell 537 crystal.

4. DISCUSSION

The experimental results reported here seem to agree in general with the existing model for thermoluminescence.[10] A short and simplified summary of which follows.

Localized energy levels are assumed to be located in the forbidden gap between the conduction and valence bands. Those right below the conduction band serve as electron traps and those above the valence band as hole traps. X-ray irradiation fills one of these traps. When the irradiated crystal is heated, thermoluminescent glow arises from recombination of holes and electrons after their thermal release from the corresponding trapping levels. These traps are characterized, among other factors, by different activation energies. It is clear now that X-ray irradiation at RT will result in filling up traps with sufficient "depth" (activation energy) while the more shallow traps will remain unfilled. Cooling the irradiated crystal to LNT will not change this situation. Illumination of the crystal at 77°K with light absorbed in "electron trap" type color centers may result in the release of trapped electrons part of which in turn will be distributed among the available electron traps, <u>including now the shallow traps</u>. Some of the released electrons probably will be either retrapped in their original traps or recombine with trapped holes. Heating the crystal from LNT to RT will give rise to peaks characteristic of the traps that will thermally release only electrons. In a similar way one gets glow peaks characteristic of released holes when the illumination is confined to "hole trap" type color centers.

In the Ge-doped quartz the ~ 280 mμ absorption bands are postulated to be due to electrons trapped at substitutional germanium atoms.[11]

The fact that illumination only in the ~ 280 mμ band, (Fig. 3), was found efficient in re-exciting almost all the glow peaks - except the one at 257°K (Figs. 1 and 2) - shows, that the main glow peaks in Ge-doped quartz are due to thermally released electrons. The 257°K-glow peak seems to be due to thermally released holes, since illumination in the 440-mμ band only is efficient in re-exciting this peak and since the ~ 440 mμ bands are attributed to trapped holes.[12] This implies the existence of a "hole trap" type center in Ge-doped quartz, which bleaches out thermally at about 257°K. These results seem to agree, at least qualitatively, with e.s.r. measurements of Mackey[13] on Ge-doped quartz, who also detected the existence of a hole trapping center in Ge-doped quartz bleaching out thermally in the temperature range 220-250°K.

The results as shown in Figure 4 imply that electrons are transferred from deeper traps to shallower ones merely by keeping the crystal in the dark for a long enough period of time. In the Ge-doped crystal we see that this type of electron re-distribution takes place between the 600°, 460°, and 410°K peaks only, whereas the 368°K peak though most intense in the illumination re-excited glow (Fig. 2) does not appear in Figure 4 at all. An explanation consistent with this might be that the electronic traps corresponding to the 600°, 460°, and 410°K glow peaks are in close proximity. Also, the rather close connection between the traps associated with the 600° and 460°K glow peaks seems to be supported by results of recently[14] reported thermal annealing measurements. It seems worth noting at this point, that the present type of measurements do not furnish us with much information concerning the highest temperature glow peak at 600°K. From recent measurements,[15] however, it became evident that this peak is complex and consists of at least three different component peaks.

In the Ge-free crystals, again, the ~ 440 mμ bands are interpreted in the same way as in the case of the Ge-doped ones. Namely these bands are attributed to trapped holes.[12]

As for the electron-type centers these have not been detected hitherto, neither by optical nor by ESR measurements. Little doubt, however, remains about the fact that the overall increase in optical density in the UV after X-ray irradiation of these crystals, is due to such centers, since illumination in the UV re-excites the different peaks from those re-excited by the ~ 440 mμ bands.

Another interesting point is the rather weak shoulder at 280 mμ in the re-excitation efficiency curve (Fig. 6) of the Bell 537 (nominally Ge-free) crystal. That this shoulder is indeed an indication of the presence of traces of Ge in this crystal is supported by the fact that in the case of the Madagascar rose quartz (the experimental results of which are not discussed in detail in the present work) the corresponding curve shows an even more pronounced shoulder at the same wavelength. Inspection of Table I shows that the rose quartz does, apparently, contain a higher concentration of Ge. The possibility of tracing the presence of small concentrations of Ge which are almost undetectable by other means, proves once again the power of the present effect.

As seen from Figure 5, the main sub-RT glow peaks in the 537 crystal are associated with electron traps, except the one at about 220°K. The fact that one is unable to re-excite glow peaks above RT in this crystal might be due to the fact that the peaks right above RT are associated with the near UV color centers which after heating the crystal to about 400°K bleach out. Since illumination in the hole ~ 440 mμ band was also ineffective in re-exciting any of the above RT peaks (although after such bleaching the said band did diminish in intensity) while even after heating to as high as 500°K the 220°K hole peak is still excitable, one

can conclude reasonably well that in the Bell 537 crystal the peaks between RT and 500°K are due to thermally released electrons.

It seems quite clear that the close relation between various absorption centers induced by X-ray irradiation and thermal glow is fairly established. This appears to be in contrast with Medlin's conclusion[6] that there is no connection between the two phenomena in natural crystals.

It seems also doubtful whether Medlin succeeded in his efforts to introduce various impurities into his crystals, since we do find, at least in the case of Ge, that this impurity does affect the glow curves obtained, markedly (see also Reference 7).

CONCLUDING REMARKS

The method used in the present paper proved itself useful in quartz as it has been found useful in the case of alkali halides.[9]

It should be interesting to use this method for re-exciting magnetic color centers and, thus, gain more insight into the nature of their correlation to the optical centers. These kind of measurements are now under preparation in our laboratory.

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Captions to Figures

Figure 1: Glow curves in the range [LNT to RT] for the Clevite Ge-doped crystal.

(a) "X-Glow": X-ray irradiation for 20 minutes at LNT.

(b) Re-excited glow: X-ray irradiation for 20 minutes at RT followed by illumination, at LNT, with λ = 280 mμ for 15 minutes.

Figure 2: Glow curves in the temperature range 300°K - 500°K, Clevite Ge-doped crystal.

(a) "X-Glow": X-ray irradiation at RT for 10 minutes.

(b) Re-excited glow: X-ray irradiation at RT for 10 minutes, heating up to 500°K, cooling to RT and illuminating with λ = 280 mμ for 10 minutes at RT (3 x enhanced scale).

Figure 3: (a) Intensity of the re-excited glow peak at 368°K as a function of wavelength of the illuminating light. Clevite Ge-doped crystal.

(b) X-ray induced absorption bands, for comparison with (a). In both curves X-ray irradiation was carried out for 30 minutes.

Figure 4: "Thermal" re-excitation in the Clevite Ge-doped crystal.

(a) Results of heating up again, the X-ray (at RT) colored crystal immediately after cooling it to RT.

(b) As curve (a) but keeping the crystal in the dark for 17 hours at RT before heating it up for the second time.

Figure 5: A sequence of glow-curves obtained from the Bell 537 Ge-free crystal, in the temperature range LNT to RT, according to the following schedule:

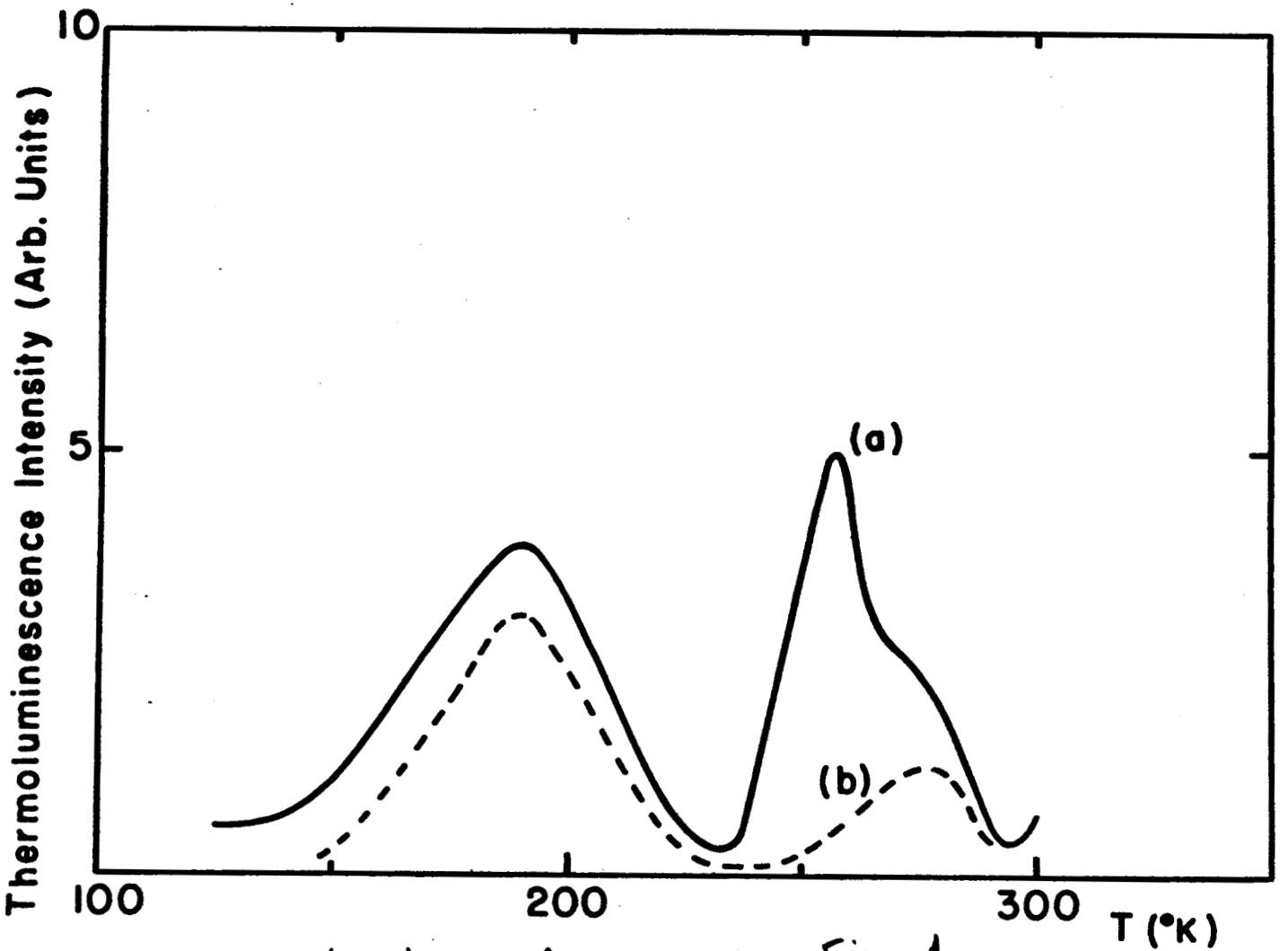
(a) After a 10-minute X-ray irradiation at LNT [reduced 50 times] this step included an actual heating up of the crystal to 650°K.

(b) 10 minutes after (a) was completed, the crystal was irradiated with X-rays for 10 minutes at RT, then immediately cooled to LNT, exposed to 280 mμ light for 15 minutes, and then curve (b) obtained.

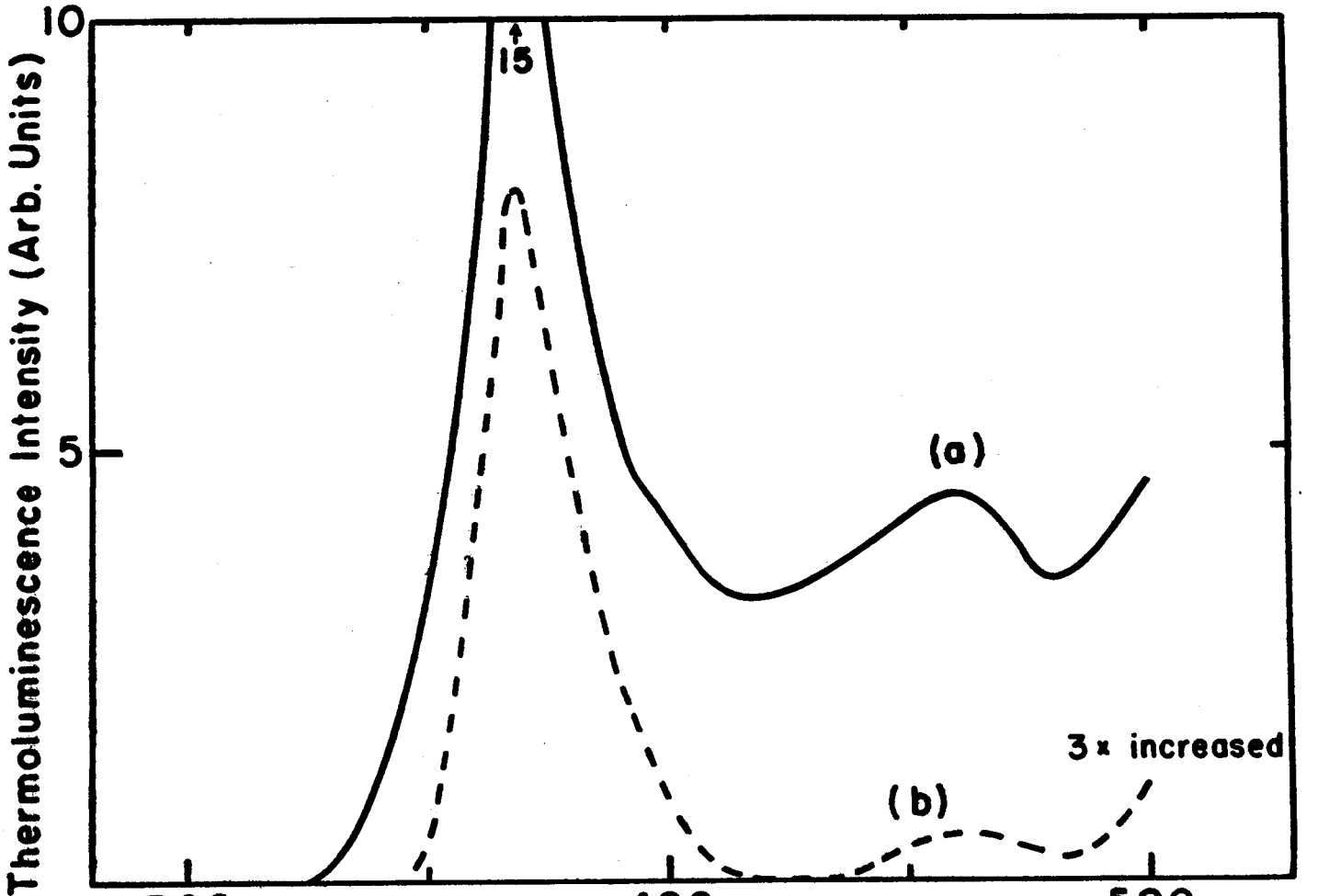
(c) 10 minutes after curve (b) was obtained step (b) was repeated except that 435 mμ light was used.

Figure 6: The relative intensities of the re-excited glow peak at 190°K as a function of the wavelength of the illuminating light in the Bell 537 crystal.

Figure 7: Regular glow curve (X-Glow) for the Bell 537 crystal in the region above RT: X-ray irradiation at RT for 10 minutes.



Mordechay Schlesinger Fig 1



Mordechay Schlesinger Fig 2

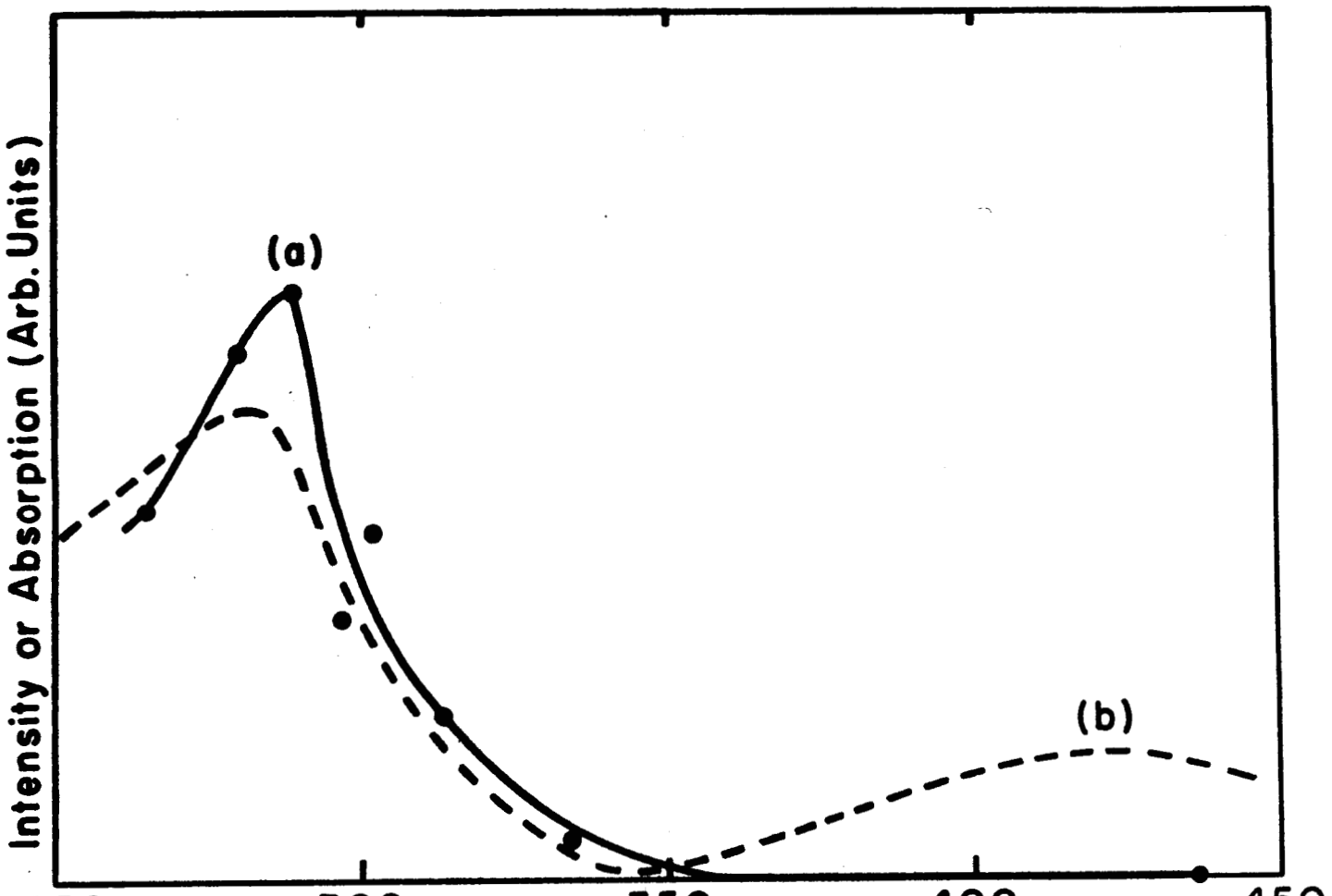


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Fig 3

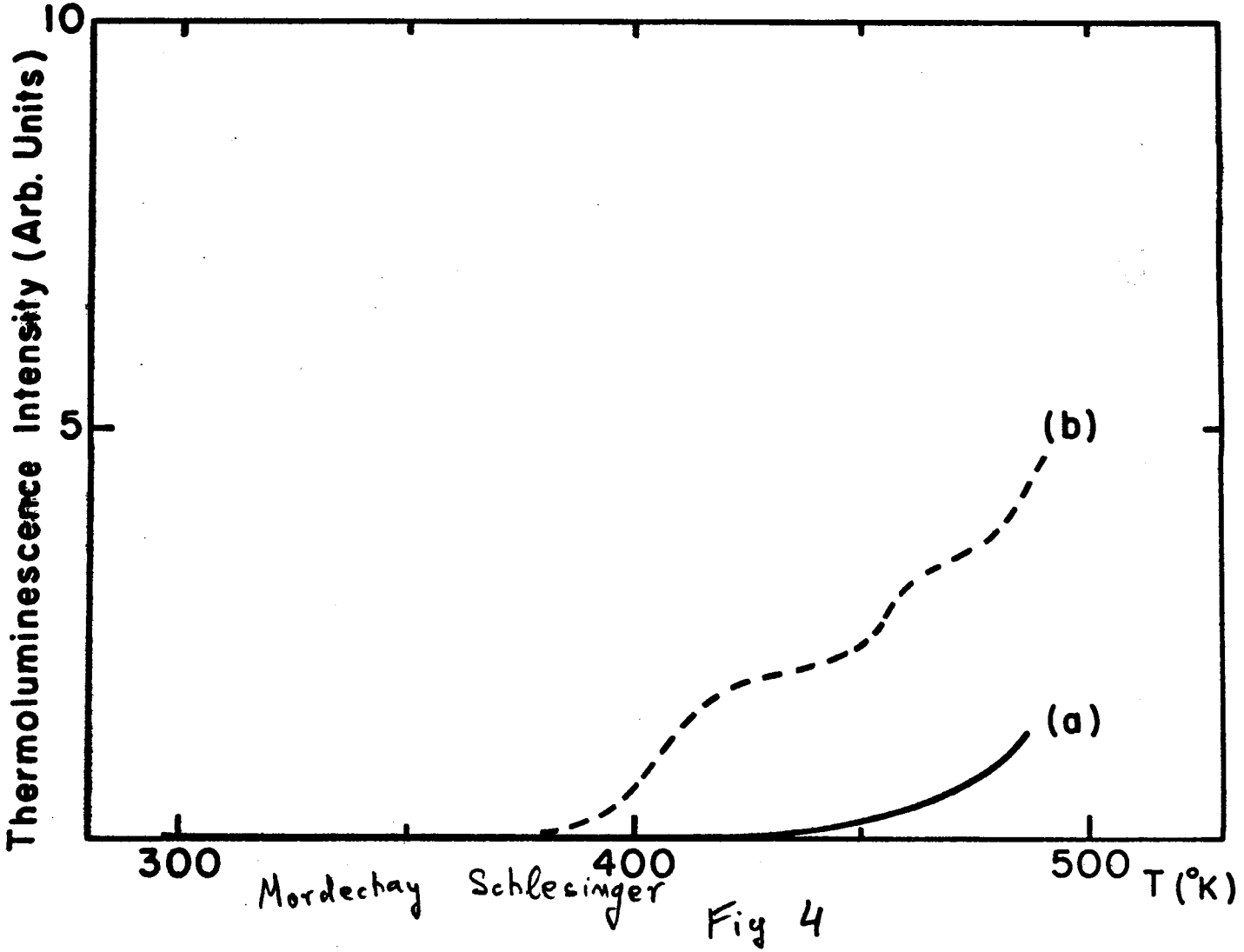

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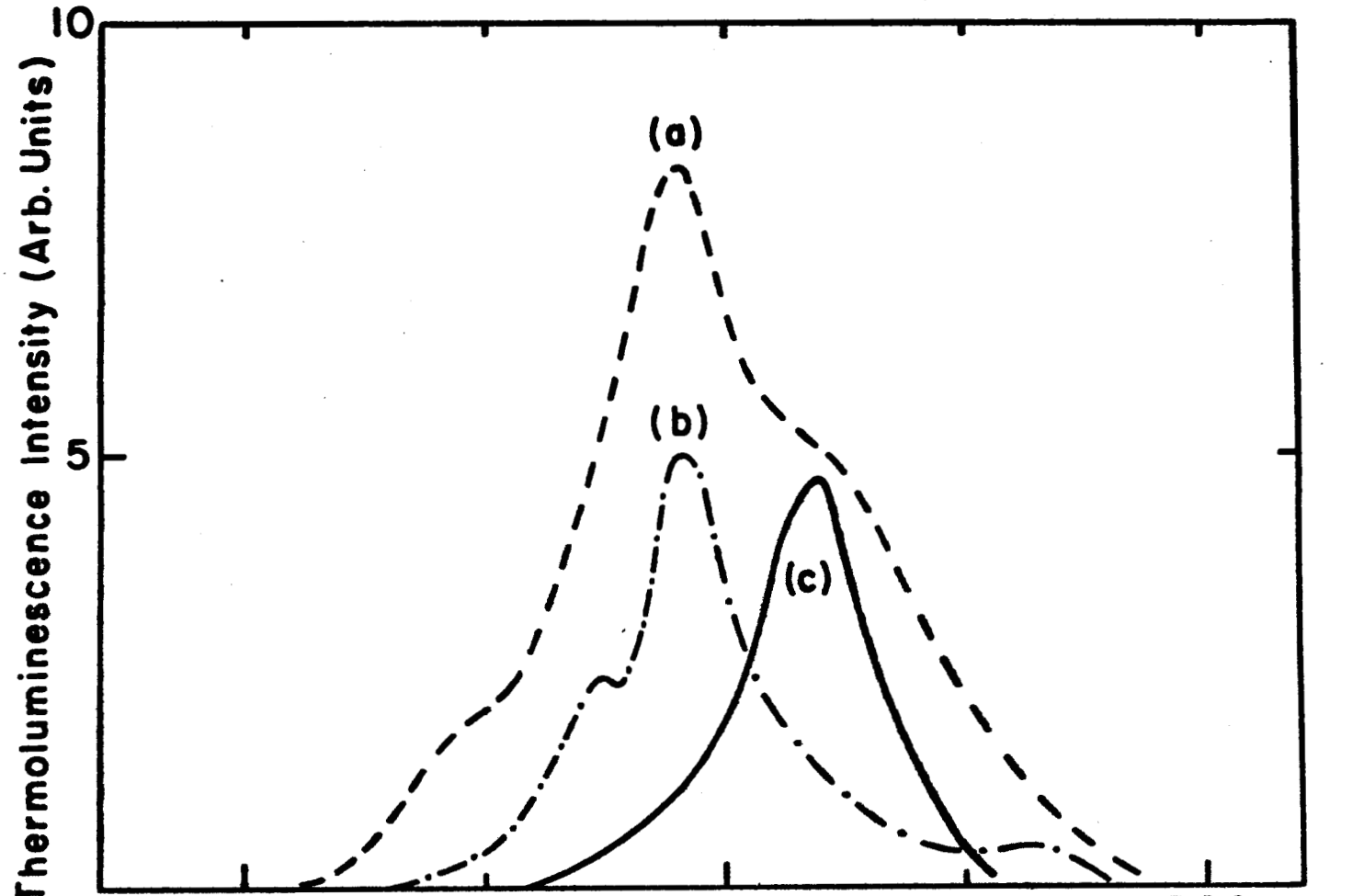
Fig 4



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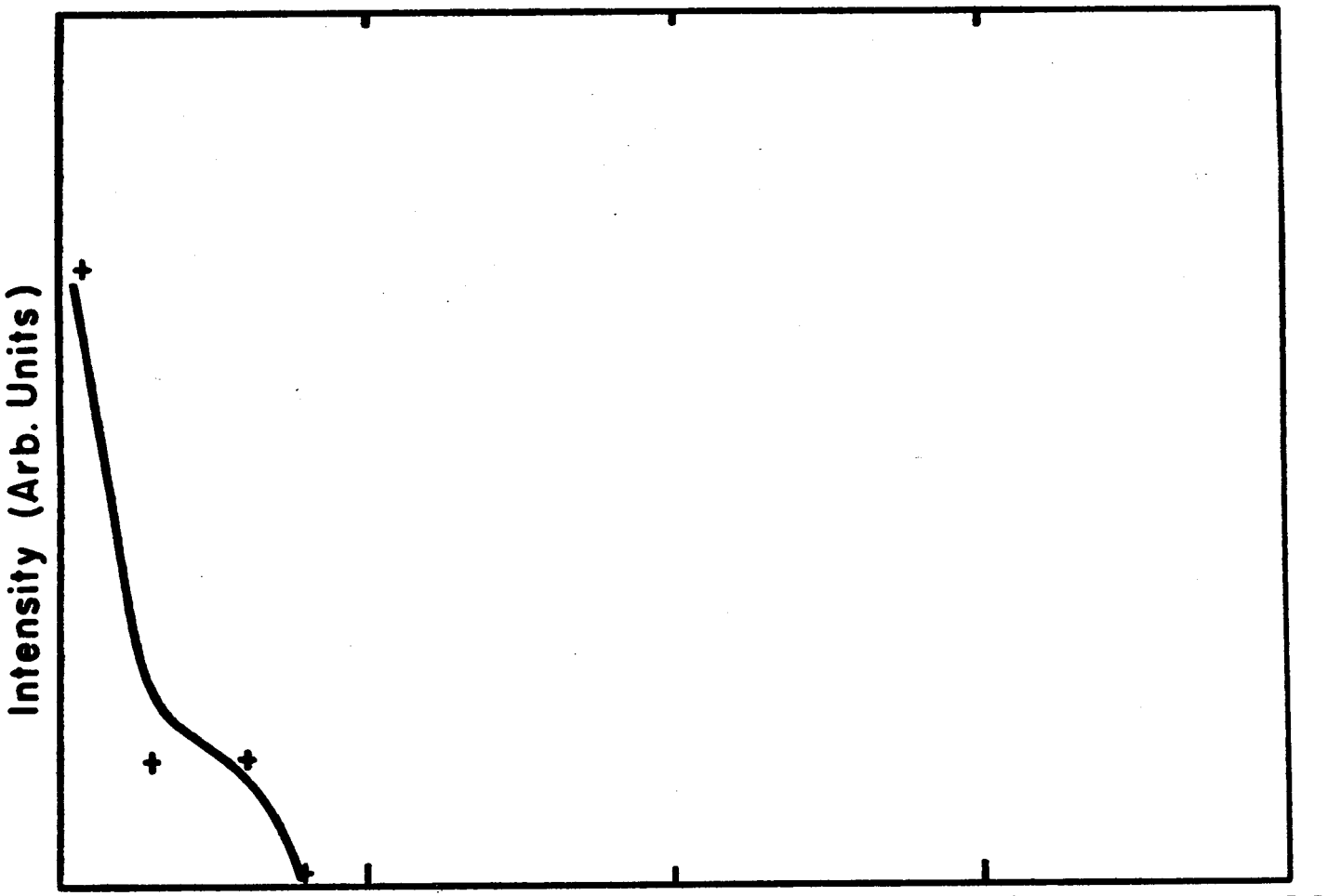

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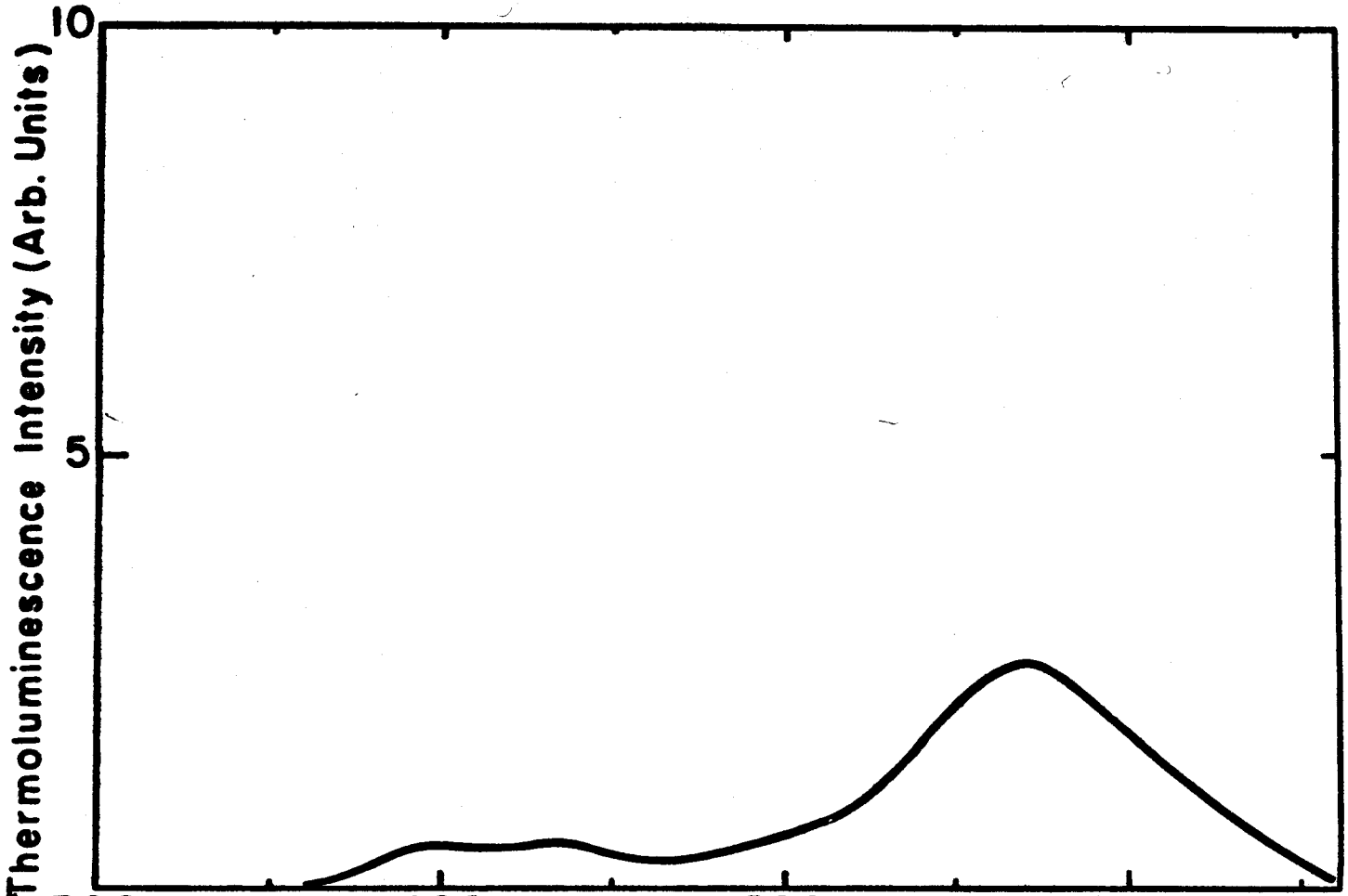

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Fig 7