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CONTRACT : AF 61 (052)- 328

OBJECTIVE OF THE WORK: Experiments on Thermoluminescence

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TITLE : "Further measurements of NaCl thermoluminescence parameters and related topics".

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SUMMARY

The Authors report the results of new measurements of NaCl thermoluminescence parameters. Such measurements have been carried out by means of the new apparatus already described in a previous Techn. Note.

The results obtained consist of the new value of the activation energy, which is confirmed as being common for all the glow peaks above room temperature and which amounts to E = 1.25 eV; besides, in the new values for the probability factors p_i, which come out to be strongly increased as compared to former measurements.

Using these new values of E and of the p_i's, the Authors repeated the calculations relative to the isothermal bleaching of F-Centers , obtaining results which are not notably different from those reported in a previous Techn.Note.

It has, moreover, been observed in a different temperature range an optical re-excitation effect of glow peaks similar to that observed by other authors at low temperature.

A discussion is given of this topic.

1. - NEW MEASUREMENTS OF ACTIVATION ENERGY.

The reader is supposed to be familiar with the content of our previous work on thermoluminescence (TL) of alkali halides [1] and on its implications, such as isothermal bleaching calculation [2]. Also, he is referred to previous work dealing with some criticism raised against our work on TL of X-ray colored alkali halides above room temperature [3] as well as to our reply [4].

We limit ourselves ,here, to remembering that one of the main arguments on which Halperin's criticism was based and which contributed to throw some doubt on the validity of our point of view was concerned with the fact that according to Halperin's results, and opposite to our own results as well as those by Hill and Schwed [5], the three (or four) peaks of light

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1) a : Technical Notes No. 1b)2b)3b) -Contract AF 61 (514)-1333.
   b : Final Report b)-Contract AF 61 (514)-1333.
   c : G.Bonfiglioli, P.Brovetto,C.Cortese:Thermoluminescence and F-Centers I(Theory) and II (Experimental),Phys. Rev. 114,951,1959.

2) : Technical Note No. 3d)-Contract No. AF 61(514)-1333.

3) : Halperin and Braner,Phys.Rev. 117, 408-416(1960).
   Halperin,Kristianpoller,Benzvi, Phys.Rev. 116,1081(1959).

4) : Proceedings of the International Conference on Color Centers and Crystal Luminescence - Torino Sept. 1960.

5) : J.J.Hill and Schwed, J.Chem. Phys. 23, 652 (1955).

shown above room temperature by NaCl did not exhibit a common value of the activation energy E, but more than one.

Actually we found in our early work only one value of E, namely 0.72 eV; but our confidence in this numerical value was actually poor, for several reasons already pointed out(1b). Moreover, our value differed sensibly from the value quoted by Hill and Schwed (E = 1.28 eV). As a consequence of this error, the values of the probability factors too were expected to be incorrect, and this circumstance in its turn compelled us to revise also this point.

With the aim of clarifying the doubts just recalled, we have thought it necessary to repeat the measurements under improved conditions. We have therefore built up a new apparatus, already described elsewhere (6), whose main characteristics consist in the use of a synchronous rectification system which, eliminating practically the noise, allows a very high sensitivity and a good linearity of response vs. the signal amplitude. Besides, an electro-mechanical control of the heating speed, makes it constant to better than 1%.

All these precautions have therefore enabled us to strongly improve the accuracy of the measurements as compared with the old setup.

As to the details concerned with the processing of the experimental data, once the reader has been referred to

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6) a : Summary Report -Part A - ARDC Contract No. AF 61(052)-328.

b : G.Bonfiglioli, P.Brovetto, C.Cortese-Rev.Scient.Instr. 33, 1095 (1962).

the papers quoted in footnote (1),we have only to state that the method followed for evaluating the activation energy is again the method of the "initial rise" , which is the only method giving results independent by definition on any particular hypothesis on the kinetics. However, due to the higher sensitivity of our present equipment , this time we have been able to make use only of the part of each peak corresponding to less than 5% of its area.This ensures that the number of V and F-Centers recombined is small enough to justify the assumption that their total number has not moved sensibly during the rising period , which implies in turn that the rise is strictly exponential.

We point out that use has been made of two values of the heating speed , namely : $\beta_1 = 0.64$ °C sec^{-1} ; $\beta_2 = 0.2$°C $sec.^{-1}$. We have noted, as quite obvious, that the measured activation energy results <u>independent</u> of β.

The results of the measurements of E are summarized in Table I.

T A B L E I

Order of peak	I	II (°)	III
	Average taken on 4 measurements	Average taken on 6 measurements	Average taken on 7 measurements
	$\bar{E}$ = 1.21 eV	$\bar{E}$ = 1.21 eV	$\bar{E}$ = 1.27 eV
	$\delta\bar{E}$ = 0.06 eV	$\delta\bar{E}$ = 0.21 eV	$\delta\bar{E}$ = 0.03 eV

(°) First component of the "doublet".It has not been possible to measure the E of the second component, because of strong overlap.

We note at once that the standard error for the E of the second peak is much larger than for the other peaks, which is due to the considerable difficulty experienced in isolating its initial rising part. However, the average value of E for the second peak does not differ much from the others. Having thus verified that within the experimental errors we are dealing with only one activation energy, it ensues that the average common value is :

$$\bar{E} = 1.25 \text{ eV}$$

with a standard error

$$\delta\bar{E} = 0.03 \text{ eV}$$

The value obtained is practically the same as the one given in paper (5) and it is ascertained that this value is common to all the peaks above room temperature , which is in disagreement with the results of Halperin and coworkers (3)[7].

Fig. 1 reproduces 3 original records. The ordinal number of the peak is indicated , as well as the warming speed and the voltage at the photomultiplier.

Fig. 2 shows the semilogarithmic plot corresponding to

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(7) On the other hand, it is not useless to recall once more that through all this work as well as previous one , we never made use of a same specimen more than once, while Halperin and his coworkers used to recycle several times the same specimen. Apparently also Hill and Schwed chosed our same procedure and this circumstance could perhaps be of some significance.

the records of Fig. 1. From similar records the values of the activation energy given in TABLE I have been deduced.

2. - THE PROBABILITY FACTORS.

In connection with the changed value of the activation energy, we had also to reconsider the "probability factors" p_i, associated with the radiative recombinations that originate the glow peaks.

The procedure followed has already been extensively explained in papers 1a, 1b. Fig. 3 shows a record of a complete glow curve, from which the areas of the single peaks have been found.

We have verified that, trying to keep always the same irradiation conditions, one always obtaines the same areas with good approximation.

We must add that in the calculation reported here, we have still made use of the wavelenghts given by Hill and Schwed (5)[8], as characteristic of each TL peak. On the other hand, the phototube used throughout these experiments with the new apparatus was a 6810 A (RCA), having a spectral response S 11, different, therefore, from that of the 1P21 used previously. This has, of course, been taken into account, in the eva-

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8) λ_I = 3620 Å
λ_{II} = 4180 - 4320 Å
λ_{III} = 5250 Å
Cfr. also 1b and 1c).

luation of the concentrations of the luminophor centers, from the areas of the corresponding glow peaks.

The initial F-centers concentration in the crystal used to evaluate the p_i's has been measured optically assuming the oscillator strength f= 0.31 (1c). It turned out to be $n_o = 5.10^{16}$ cm^{-3}.

Table II summarizes the results relative to the probability factors.

T A B L E II

Order of peak	I	II	III
β = 0.64 °C/sec	(Average taken on 3 meaurements) $\bar{p}_1$= 3.06 cm^{3}sec^{-1} $\delta\bar{p}_1$= 0.89 cm^{3}sec^{-1}	(Average taken on 3 measurements) $\bar{p}_2$= 1.44·10^{-3}cm^{3}sec^{-1} $\delta\bar{p}_2$= 0.39·10^{-3}cm^{3}sec^{-1}	(Average taken on 3 measurements) $\bar{p}_3$=1.50·10^{-5}cm^{3}sec^{-1} $\delta\bar{p}_3$=0.03·10^{-5}cm^{3}sec^{-1}
β = 0.20 °C/sec	(Average taken on 4 measurements) $\bar{p}_1$= 3.23 cm^{3}sec^{-1} $\delta\bar{p}_1$= 0.43 cm^{3}sec^{-1}	(Average taken on 4 measurements) $\bar{p}_2$= 3.88·10^{-4}cm^{3}sec^{-1} $\delta\bar{p}_2$= 0.53·10^{-4}cm^{3}sec^{-1}	(Average taken on 4 measurements) $\bar{p}_3$= 0.42·10^{-5}cm^{3}sec^{-1} $\delta\bar{p}_3$=0.005·10^{-5}cm^{3}sec^{-1}

On can see from this table that there is a sensible dependence of p_i-S on β. However , if one considers that p_i's are

significantly different only if they differ throught many orders of magnitude (inasmuch as only in this case the TL curves are affected), one can state that the dependence on β is certainly quite weak.

Then, as to the very strong discrepancy (implying factors of the order of $10^6 \div 10^8$) of the new p_i's as compared to the values of previous work, this discrepancy is simply due to the fact that the E value has been increased by 60% , which produces in fact a decrease of a factor $10^6 \div 10^8$ on the activation factor $\exp(-E/kT)$.

Therefore, the quantities $k_i(T) = p_i \exp(-E/kT)$, which are the only "observable quantities" of these measurements, do not change appreciably.

The difficulties which bring to these very strong fluctuations in the evaluation of the probability factors are, therefore, of a purely technical nature; and on the basis of the foregoing statements, the effect of a change of β on the values of the p_i's is not surprising itself. On the other hand, one must bear in mind that our whole treatment of TL, that is to say, the use of equations which are bilinear in the concentrations of the electron and hole centers, as well as the use of an activation law with p_i factors independent of T, constitutes a first approximation , which is the one generally used in kinetics problems and which is apt to supply the substantial point of experimental facts.

Of course, one must then not be astonished when high accuracy measurements evidence slight disagreements, as it is the case with the quoted effect of β on the p_i's.

3.- ISOTHERMAL BLEACHING.

On the grounds of the new values found for E and the p_i's , the theoretical calculation of isothermal bleaching exposed in a previous Techn. Note[2] had obviously to be reconsidered. However, in agreement with the mentioned fact that the $k_i(T)$'s did not sensibly move , the new curves of isothermal bleaching did not change appreciably from the previous ones.

4.- OPTICAL REEXCITATION OF GLOW PEAKS.

In connection with the foregoing results about TL of NaCl, we expose here some result concerning the phenomenon of the optically stimulated reexcitation of the glow peaks.

A paper has recently been published on this subject[9], in which experiments are reported on NaCl crystals irradiated with X-rays at a definite temperature T_x. Stoddard reasons that so doing, those centers which are responsible of glow peaks with a maximum at a temperature $T_G < T_x$ cannot be created. In fact, carrying out a TL run starting at the temperature $T_o < T_x$, he observed no peaks up to T_x. Thereafter peaks with $T_G > T_x$ appear.

If , however, before heating is started , the crystal undergoes illumination at the inferior temperature T_o, it is in general observed that the peaks with $T_G < T_x$ actually do show themselves (optical reexcitation effect), while peaks with $T_G >$

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(9) A.G.Stoddard - Phys.Rev. 120,114 (1960).

T_x are weakened (optical bleaching effect). Moreover, these phenomena show a sharp maximum when F-light is made use of.

In Stoddard experiments , two X-rays irradiation temperatures were used namely : $T_x = -75°C$, $T_x = +100°C$, while invariably if was $T_o = -195°C$.

On these grounds Stoddard conclusions were that electrons are liberated by F-light and go to re-populate those electron traps that are responsible of the glow peaks with $T_G < T_x$.

This clearly would imply that peaks are due to the presence of more than one kind of electron traps - which would be in conflict with our model. On the other hand, the bleaching effect for peaks with $T_G > T_x$ is precisely predicted by our model , since optically released electrons necessarily recombine with a fraction of trapped holes - and in this way destroy the same fraction of the hole centers to which high temperature glow peaks are due.

Assume now that T_x is so chosen as to leave only the second glow peak ($T_G \simeq 143°C$) and third ($T_G \simeq 206°C$), for example, $T_x \simeq 120°C$. Do the peak with $T_G \simeq 65°C$ (1st peak) become reexcited , following F-light illumination? Obviously, <u>once Stoddard way of reasoning is adopted</u>, if the answer to the above question turn out to be positive, then the 1st peak should be attributed to electronic centers different from F-Centers - in disagreement with our model. If on the contrary the peak in question is due , as our model assumes, to a certain species of hole centers , (such as V-centers) , in this case an optically stimulated reexcitation could actually be expected, <u>but</u> only by using light in the absorption band of some V center.

Actually , there are available experimental evidencies that Stoddard reasoning is too naive - as we shall show later on[10].

However, since the mechanism of optical reexcitation is not fully understood, we made the experiment, hoping that our experimental data may become useful fur future interpretation.

We found reexcitation of peak with $T_G \simeq 65°C$, but unfortunately, we have not been able to check accurately the behavior of this phenomenon as a function of the wavelenght.

The measurements have been carried out using as a light source a fluorescent lamp (Mazda 4 W Blue General Electric) followed by an interferential filter whose azimuth could be varied between 0° and 45°C.

In this way we had available the wavelenghts ranging from 4320 Å to 5160 Å. The bandwidth was around 150 Å. Moreover, using a tungsten filament lamp and a red interferential filter (λ=6350 Å) we made available wavelenghts beyond 6000 Å.

All these spectra have been recorded using a Hilgher glass spectrometer followed by a 1P21 photomultiplier. Corrections were made for the phototube response and for the spectrometer dispersion. In this way we normalized all the luminous intensities (in number of photons rather than in energy).

The specimens were irradiated with our X-rays generator at room temperature ; then they were linearly heated, up to 200 °C in our TL apparatus, so as to be sure that every previous glow peak has been suppressed. This technique is clearly equivalent to irradiate the specimen at 200°C - and gives the certainty that only the highest T_G peak is still present when the specimen is illuminated. This was done at room temperature with

monochromatic light - as explained above - for a period of 20 minutes.

The estimated order of magnitude of the integrated photon flux per unit area was : 10^{20} photons/cm^2 .

Finally , a TL run was repeated, and the reexcitation of peaks verified. Fig.4 shows the record of some runs, showing clearly the presence of a reexcited peak, more or less pronounced,according to the value of the illuminating wavelenght.

Fig. 5 synthetizes the results, by showing the ratios between the height of each reexcited peak and the height of the same peak as obtained during the first linear heating, before illumination. Obviously , these ratios are normalized to a constant photon flux for each wavelenght. A different slice of a same crystalline block was used for each wavelenght. It can be seen that the effect is completely lacking for $\lambda >$ 6000 Å (red light) whilst it is substantial down λ = 4550 Å.

However, the scattering of the experimental points forbids to detect a possible resonance on F-light. This scattering of the measurements is due to bad reproducibility which we attribute tentatively to the circumstance that optical reexcitation, at room temperature, is strongly structure sensitive. At any rate, we saw that F-light was able to produce reexcitation.Whether we have a maximum in this spectral region or at a still shorter wavelenght (V_3 band) is undecided.

Let us however point out that special cares should be used to surely identify reexcited peaks - and this has not been made by Stoddard nor by the present Authors.

In fact, it is time now to rise the announced essen-

tial criticism against Stoddard interpretation. It can be stated precisely that it is to be excluded that bleaching or reexcitation depend purely on a passage of electrons from F-centers to other electron traps. This statement rests on the analysis of some experimental results which has been known for a long time (Duering and Markham,Markham, Teegarden and Maurer).

A more recent result can be found in a paper by Crawford [10] where it is reported that, by illuminating with F-light(at 195°K) a pure KCl crystal colored by ionizing radiation (at 35°C) it is observed (at 78°K) not only the obvious (strong) bleaching of the F absorption band,but, in addition, a reexcitation of the band due to the $\langle 100 \rangle Cl_2^-$ center (V_K Center of Kanzig) and a sensible bleaching of the V_3 band. Let us stress the fact that the V_K Center is <u>not</u> an electronic trap; so this result proves that it cannot be generally assumed that F-light illumination can repopulate only electronic traps. On the grounds of the model offered by Crawford (ibidem) to interpret F-Centers production, the result just mentioned can besides be justified.

Therefore , experiments like those of Stoddard do not possess the crucial character that could be expected at first sight.

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(10) J.H.Crawford,Proceed. Int.Conf.on Color Centers and Crystal Luminescence,Torino,1960,pg.21 ff.fig.5,Table V.

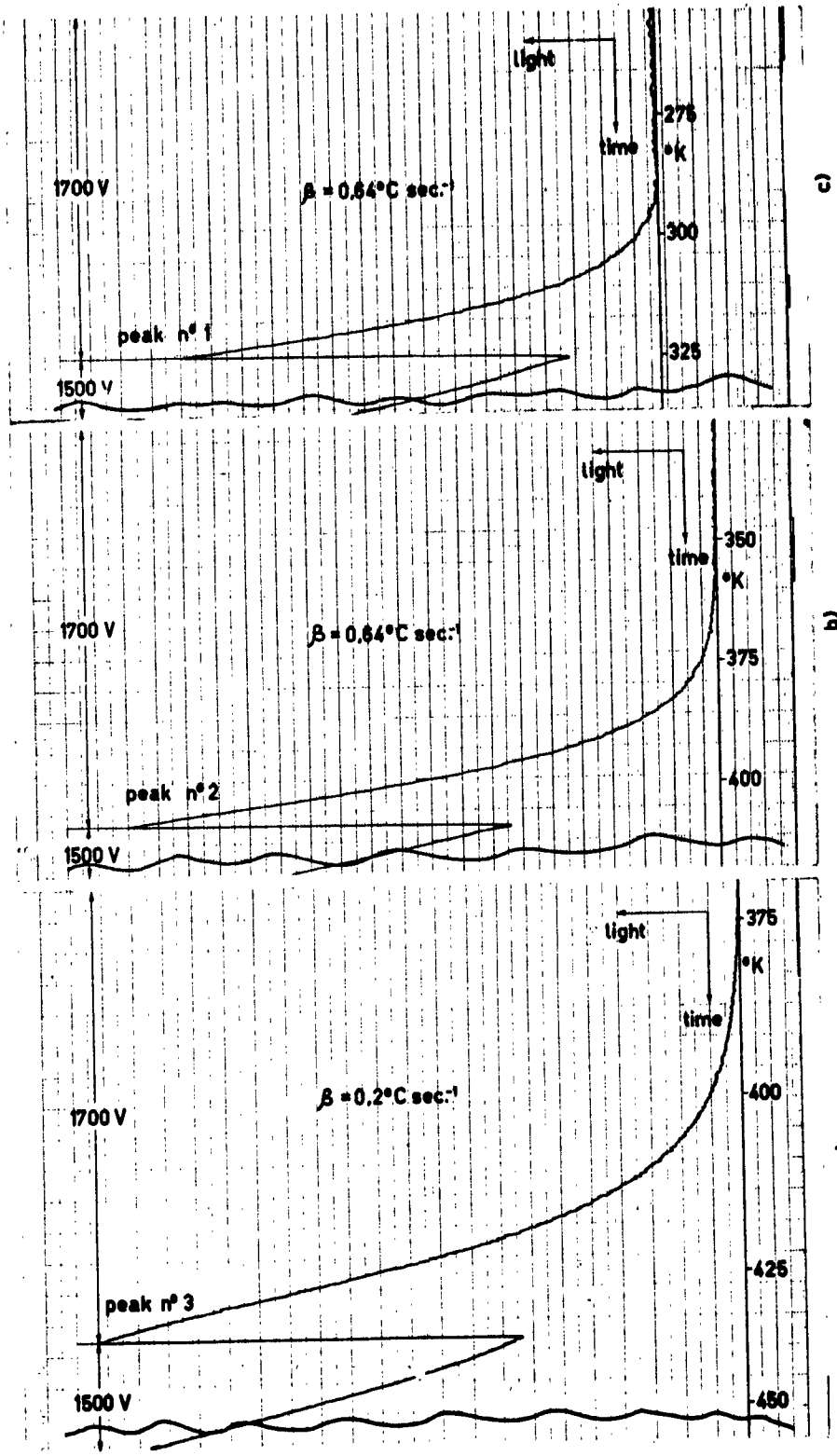
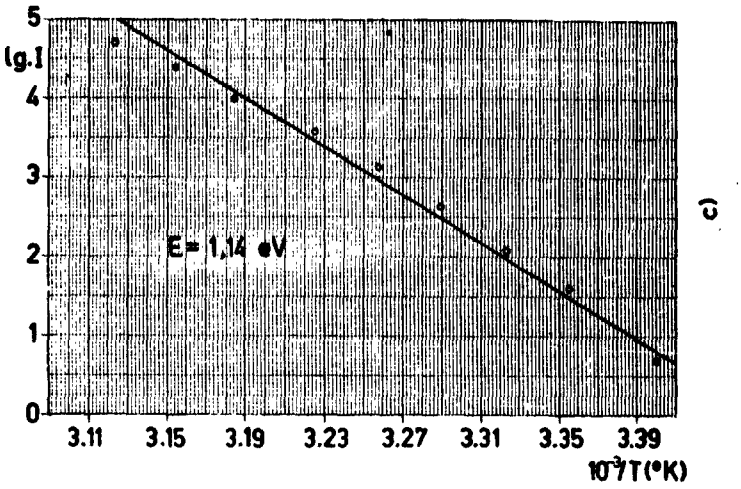
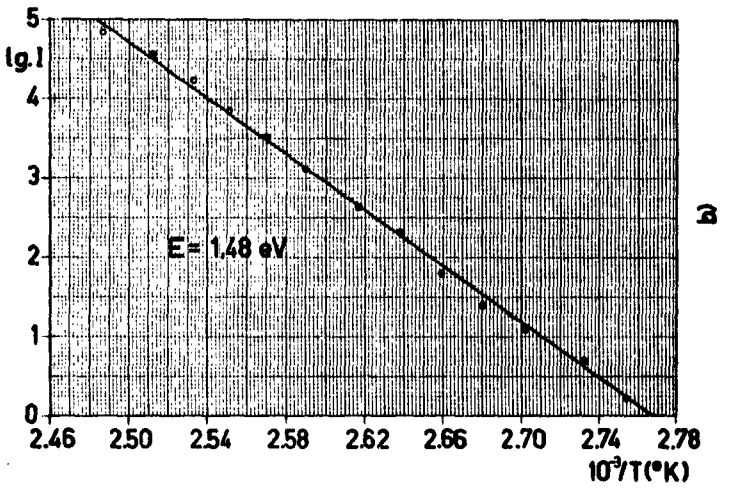

light
time
275
°K
300
325
1700 V
β = 0,64°C sec.⁻¹
peak n° 1
1500 V
c)
light
time
350
°K
375
400
1700 V
β = 0,64°C sec.⁻¹
peak n° 2
1500 V
b)
light
375
°K
time
400
425
450
1700 V
β = 0,2°C sec.⁻¹
peak n° 3
1500 V
a)

FIG. 1


lg.I
5
4
3
2
1
0
E= 1,14 eV
3.11
3.15
3.19
3.23
3.27
3.31
3.35
3.39
10³/T(°K)
c)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5
4
3
2
1
0
E= 1,48 eV
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2.54
2.58
2.62
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2.78
10³/T(°K)
b)

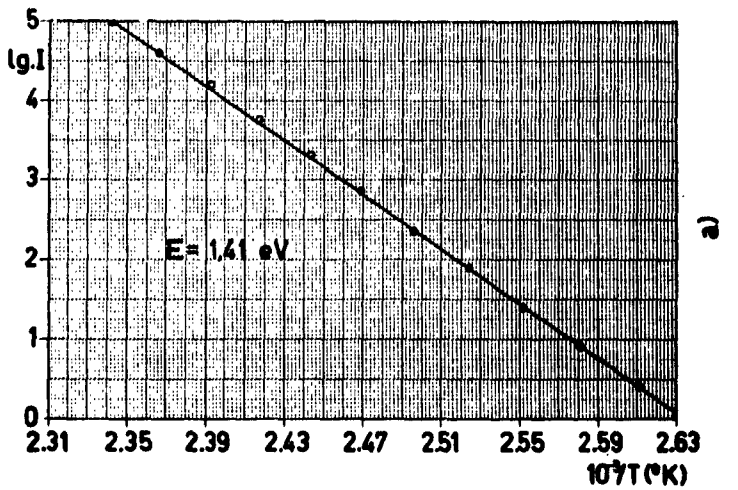
lg.I
5
4
3
2
1
0
E= 1,41 eV
2.31
2.35
2.39
2.43
2.47
2.51
2.55
2.59
2.63
10³/T(°K)
a)

FIG. 2

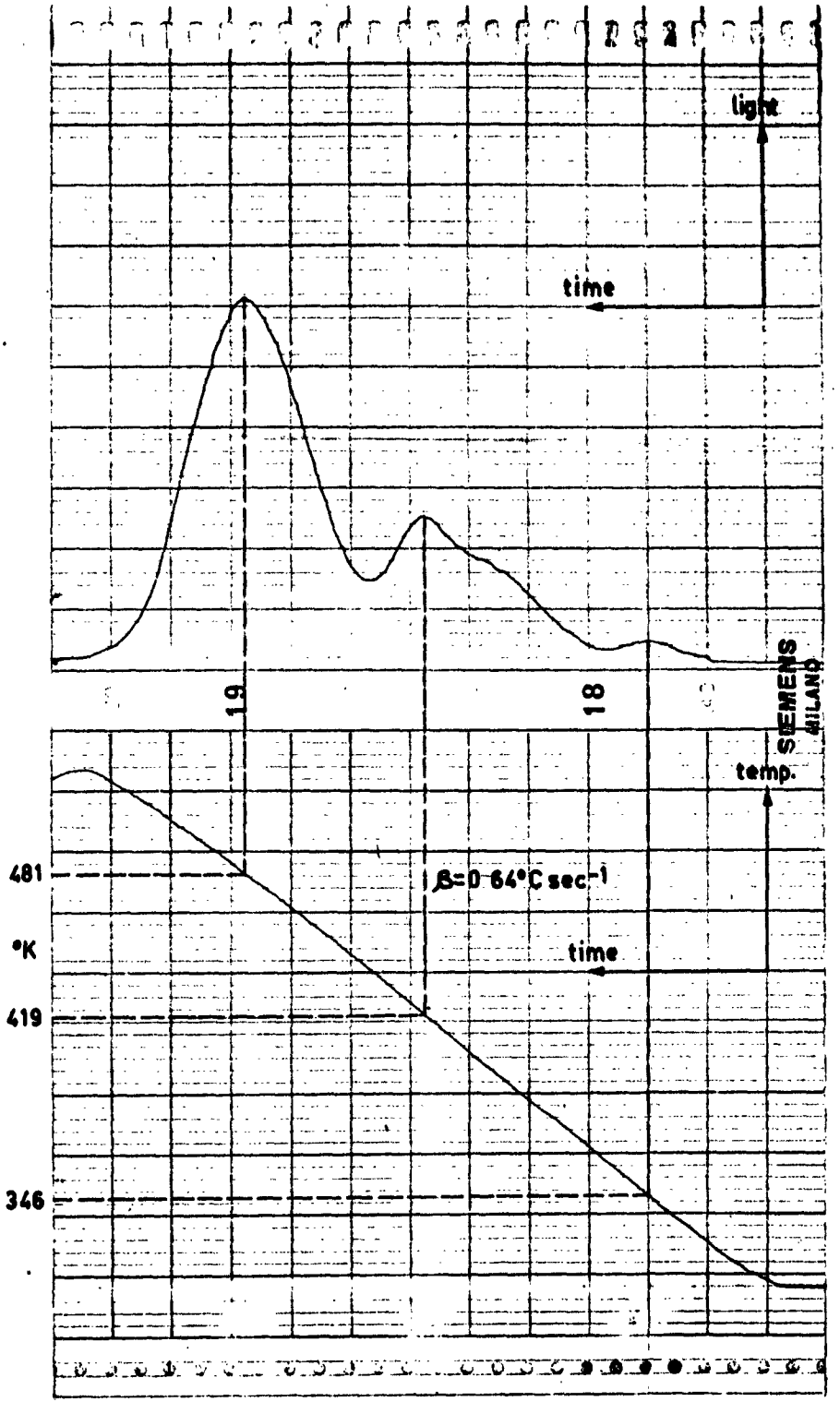
light
time
19
18
SIEMENS MILANO
temp.
481
°K
419
346
β=0·64°C sec⁻¹
time

fig. 3

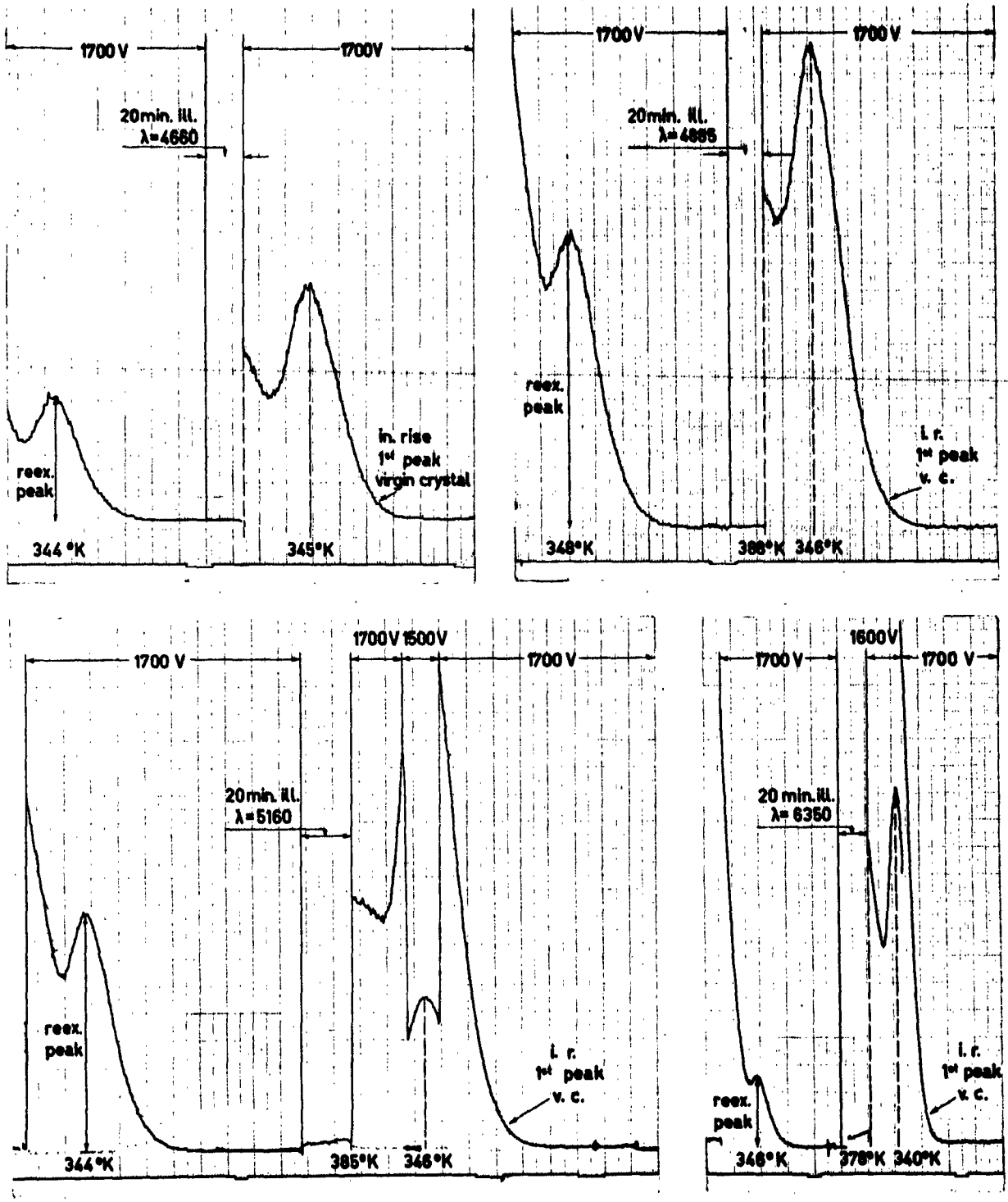
1700 V
1700V
20min. ill.
λ=4660
reex.
peak
in. rise
1st peak
virgin crystal
344 °K
345°K
1700 V
1700 V
20min. ill.
λ=4865
reex.
peak
i. r.
1st peak
v. c.
348°K
388°K 346°K
1700 V
1700 V 1500 V
1700 V
20min. ill.
λ=5160
reex.
peak
i. r.
1st peak
v. c.
344°K
385°K
346°K
1700 V
1600 V
1700 V
20 min. ill.
λ=6350
reex.
peak
i. r.
1st peak
v. c.
346°K
378°K 340°K

FIG. 4

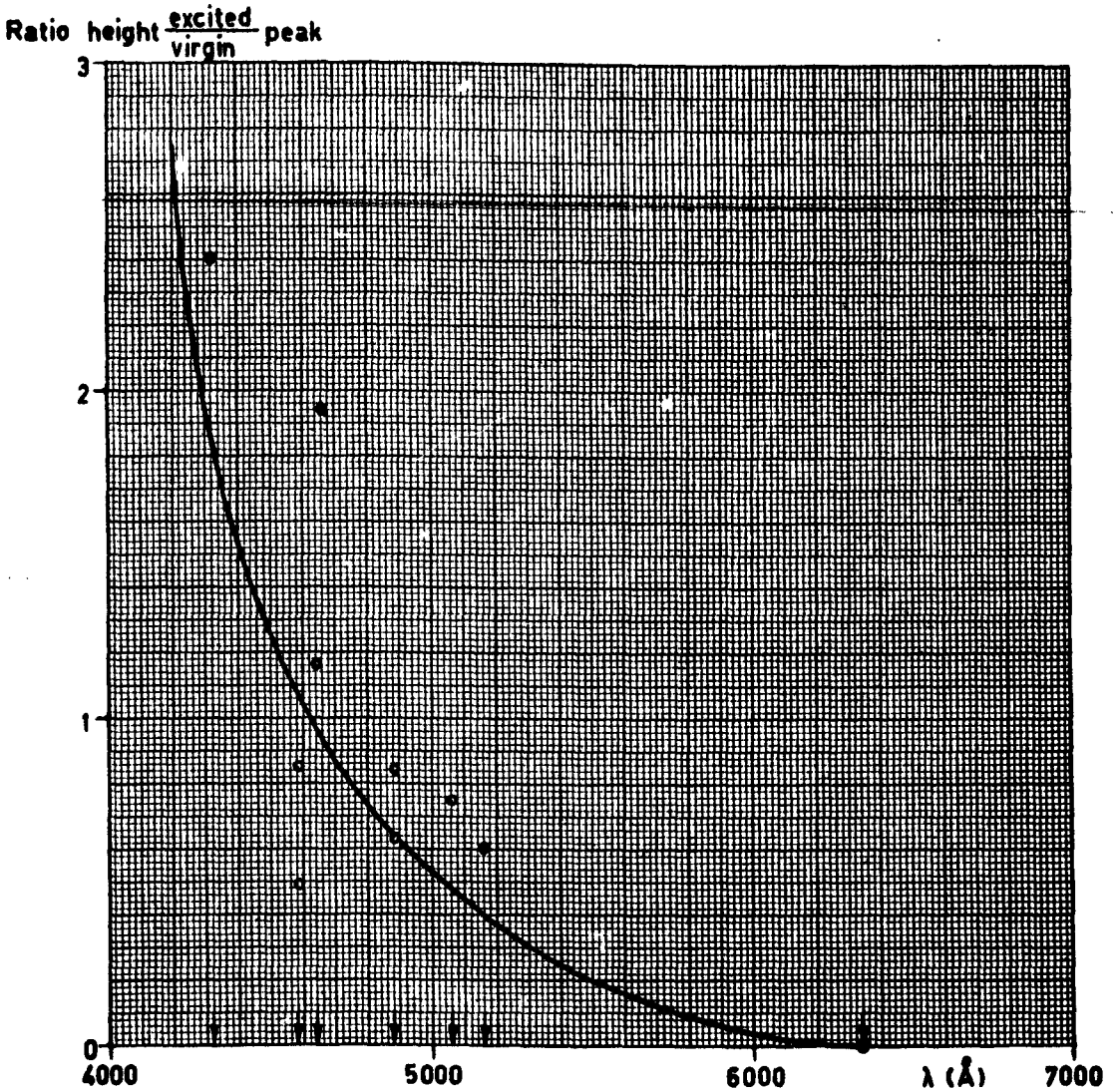
Ratio height excited/virgin peak
3
2
1
0
4000
5000
6000
λ (Å)
7000

FIG. 5