Effect of Infrared Irradiation on ZnS:Cu Phosphors*

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Infrared stimulation and quenching of ZnS:Cu phosphors are studied as a function of trap population. It is found that stimulation at low temperature increases linearly with the concentration of ionized activators and disappears when the shallowest traps are emptied. Quenching increases as the product of the concentrations of ionized activators and trapped electrons. From these results it is concluded that the main action of infrared on these phosphors is a shifting of holes to levels of higher recombination rate. This model accounts quantitatively for the dependence of stimulation and quenching on the state of excitation. It is strongly supported by infrared effects on the glow and photoconductivity and the similarity of the wavelength dependence of stimulation and quenching. Thus the light stimulation observed under infrared irradiation is not due to the usual assumption of a direct release of trapped electrons by infrared, but rather to a shifting of holes to levels of higher recombination rate.

INTRODUCTION

THIS investigation is based on the early observation that stimulation of light by infrared irradiation at the temperature of liquid nitrogen shows two ranges of strong effects when measured as a function of the ir wavelength. One is found at about 7000 A and the other at about 13 000 A, with a minimum at about 10 000 A.[1] The wavelengths of these two ranges are not too strongly dependent upon the composition and activation of the phosphors. At the same time ir of a wavelength of about 7000 A induces nonradiative transitions (quenching) at low temperature. Quenching at room temperature exhibits the same wavelength dependence as light stimulation at low temperature. This similarity between the stimulation and quenching spectra leads to the idea that quenching is brought about by the same primary process as stimulation. If the stimulation process were a release of trapped electrons into the conduction band, it would be rather difficult to understand the quenching process and account for the similarity of the spectra.

The idea that stimulation in ZnS:Cu phosphors is not due to a release of trapped electrons into the conduction band, is further strengthened by the general observation that under both long- and short-wavelength ir irradiation ($\lambda = 13\,000$ A and 7000 A, respectively) at room and liquid nitrogen temperatures, light stimulation during the phosphorescence period does not set in simultaneously with the ir radiation but is delayed considerably.[2,3] This delay is particularly large when the phosphor has been allowed to decay for days or months in the dark at room temperature prior to ir application. Delays of more than 20 minutes were found. This delay would be difficult to account for if the process of stimulation would consist of a direct release of electrons from traps into the conduction band.

It was also observed that the photoconductivity of various phosphors is decreased by ir irradiation after a transient increase and that this decrease exhibits the same wavelength dependence as light stimulation.[4,5] If the stimulation consists mainly of a release of trapped electrons, it cannot be seen why the photoconductivity during ir irradiation finally reaches a lower value than in the absence of ir, whereas the luminescence in some cases reaches an equilibrium value which is the same, or slightly larger, than in the absence of ir (see Appendix A).

These observations make it advisable to investigate the influence of ir at low temperature in more detail and to attempt to find a correlation between trap population, glow emission, and photoconductivity, and to determine the rate of radiative and nonradiative recombinations induced by ir.

2. EXPERIMENTAL METHODS AND RESULTS

The experiments described were performed on a ZnS:Cu (*MS* 17) and on a highly stimulable ZnS:Cu,Pb (2150) phosphor, both powdered. Excitation in all cases was light with 435 mμ which produces activator-band excitation in Cu-activated phosphors. The intensity was of the order of 1–10 ($\mu W/\text{cm}^2$). The ir radiation used was 760 mμ, denoted as s-ir and 1300 mμ, denoted as l-ir. The ir intensity is discussed below. The equipment used was previously described.[1]

A. Relation between Stimulation Peak Heights and Trap Population

The stimulation peak height observed during excitation is a measure of the ir-induced radiative recombinations and is characteristic of the trap population at which ir is applied. Different trap populations are attained by exciting the de-excited phosphor for different

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[1] S. Shionoya, H. Kallmann, and B. Kramer, Phys. Rev. **121**, 1607 (1961). See this article for additional references.

[2] M. Sidran, Doctoral thesis, New York University, 1955 (unpublished).

[3] H. Kallmann, J. phys. radium **17**, 787 (1956).

[4] H. Kallmann, B. Kramer, and A. Perlmutter, Phys. Rev. **99**, 391 (1955).

[5] I. Broser and R. Broser-Warminsky, Z. Elektrochem. **61**, 209 (1957).

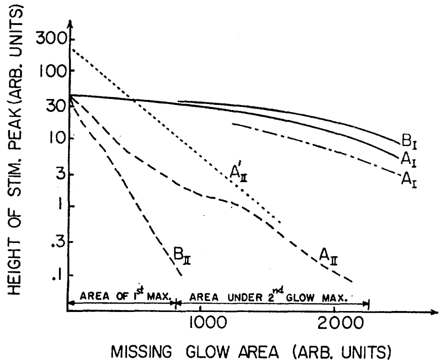

FIG. 1. Stimulation peaks of *MS*17 as a function of missing glow area: Subscript I means obtained by method I; subscript II means obtained by method II; curves A obtained with s-ir; curves B obtained by l-ir.

lengths of time. The glow area measured after a particular duration of excitation is a measure of the number of trapped electrons. Therefore the relationship between the height of the stimulation peak and the total glow area obtained at this state of excitation was studied.[6] Nonradiative transitions during the glow-curve may be neglected as a first approximation, since the phosphors used show a high efficiency during excitation and since their glow has an even higher efficiency as shown by Shionoya *et al.*[1]

The (ir) stimulation peaks, obtained after exciting in this manner, are plotted in Fig. 1, curves A_I and B_I.[7] The abscissa gives not the glow area, but the difference between the glow area obtained after excitation to equilibrium and that obtained after that degree of excitation at which the stimulation is measured. This difference is called the missing glow area. If the phosphor is excited to equilibrium, the glow area is 3000 (arbitrary units) and the missing glow area is 0. If the phosphor is not excited at all, the glow area is 0 and the missing glow area is 3000. The ordinate gives the height of the stimulation peaks in a logarithmic scale. The solid curves A_I and B_I were obtained by using s-ir and l-ir, respectively, both while the exciting light remained on. (The glow areas had been measured previously.) The broken curve A_I was obtained by using s-ir shortly after the excitation was turned off. The excitation method used in these experiments, namely that which starts with a de-excited phosphor which is excited for different periods of time, is called method I.

There is another method, which may be used to obtain the same glow areas as obtained with method I. This latter method, used by Hoogenstraaten,[8] we call method II. In this method one begins with the phosphor excited to equilibrium. Then the excitation is turned off and the temperature raised. One does not however, take a full glow curve, but stops after a certain fraction of the glow curve has been taken. Then the phosphor is recooled to the temperature of liquid nitrogen. In this case the glow area observed is identical to the missing glow area as defined above. After reaching again the temperature of liquid nitrogen, either s-ir or l-ir is applied. The stimulation peaks obtained are presented in Fig. 1, curves A_{II} and B_{II}, respectively. The area under the first glow maximum after full excitation is about 800, that under the first plus second glow maximum is about 2200. Since the phosphor was fully excited at the start, in method II, the area under the first glow maximum can be ascribed to the electrons trapped in the shallowest traps and so on for the succeeding glow peaks. Curve A_{II} shows that s-ir stimulation disappears as soon as the shallowest and medium deep traps are emptied. Curve B_{II} shows that l-ir stimulation disappears as soon as only the shallowest traps are emptied. This means that l-ir stimulation is dependent either directly or indirectly on the presence of only the shallowest trapped electrons. It is not clear however, why l-ir stimulation disappears as soon as the shallowest traps are empty, whereas s-ir stimulation seems to decrease much more slowly with trap population (curve A_{II}). It will be shown in the next section that s-ir stimulation also decays rather rapidly with trap population if the influence of quenching on these curves is taken into account (curve A_{II}').

The upper group of curves obtained by method I shows quite a different behavior from those obtained with method II. In the former, the stimulation shows only a moderate decrease throughout the curve although at large missing glow areas (=small excitation), the number of trapped electrons is small. This must mean, especially for the case shown in curve B_I, that shallow traps are occupied almost throughout the whole curve since it was shown in method II that large stimulation does not occur when the shallower traps are unpopulated. Thus a comparison of stimulation peaks obtained from phosphors excited by methods I and II shows that the shallower traps are filled first when excitation is applied to a de-excited phosphor. Since the number of conduction electrons is chiefly determined by the electrons occupying the shallow traps and not so much by those in deep traps, it can be concluded from these observations that the conduction electrons will almost reach equilibrium in the early part of the rise curve.

At a state of excitation corresponding to about half the total number of traps being filled, it is observed that in the glow curves the intensities at low tempera-

[6] Under only partial excitation, the light emitted under one glow peak may not be ascribed unambiguously to the number of electrons trapped in the more or less well-defined groups of traps of different depths. This is because electrons, originally in shallow traps, are released and retrapped by deeper traps during the heating period. Thus, starting with a de-excited phosphor and exciting for various periods of time, only the total glow area obtained after each excitation period can be used as a measure of the number of electrons trapped during this excitation period.

[7] In all cases the s-ir intensity was approximately 500 (μw/cm^2) and the l-ir intensity was approximately 2000 (μw/cm^2). These intensities were chosen to give equal stimulation peaks at full excitation.

[8] W. Hoogenstraaten, Doctoral thesis, University of Amsterdam, 1958 (unpublished).

tures are much smaller than after full excitation. This difference does not occur in the later parts of the glow curves. This would indicate that the shallow traps are not filled at partial excitation, contradicting the results found above. This apparent contradiction can be explained however, with the following simple picture. The electrons evaporating from the shallow traps which are occupied first are retrapped by deeper traps (which are not fully occupied at partial excitation) before they recombine. Thus a glow maximum corresponding to shallow traps is not seen until the excitation is extended long enough to fill deep traps as well.

B. Rate of Infrared-Induced Nonradiative and Radiative Recombinations

Up to now, only the height of the stimulation peak was discussed. In the case of stimulation with l-ir, which produces no quenching at low temperature, the height of the stimulation peak is indeed a measure of the rate of stimulated radiative transitions. In the case of stimulation with s-ir the picture is more complicated because quenching occurs concomitant with stimulation and therefore the whole stimulation area has to be investigated in order to determine the rate of stimulation. This is done in this section where quenching and stimulation are studied simultaneously for various states of excitation. The experiments give the rate of ir-induced nonradiative and radiative transitions respectively. The procedure is the following:

First the relationship between the excitation period t_i and the respective total glow areas A_{t_i} (proportional to the total number of trapped electrons n_{t_i}) is established experimentally. Then $n_{t_i}=f(t_i)$ is known. After excitation for time t_i, the excitation is removed and s-ir applied for a period T. The light area emitted during T, which is due to both phosphorescence and stimulation, is called A_{stim}. Thereafter s-ir is removed, the sample is heated, and the glow curve of area A_T is measured. The expression $A_{t_i}-(A_{\text{stim}}+A_T)$ gives the total number N_{nr} of nonradiative transitions, integrated over the s-ir irradiation time T.

$$N_{\text{nr}}=\int_0^T Qdt=A_{t_i}-(A_{\text{stim}}+A_T). \qquad (1)$$

Here Q is the rate of nonradiative transitions induced by s-ir. A plot of N_{nr} as a function of T can be obtained by repeating this procedure for various periods of time T. The derivative of this function with respect to T gives Q as a function of the time elapsed after the beginning of stimulation. The derivative for $T\to 0$ gives Q for the very first instant of s-ir action. The first instant is characterized by the state of excitation given by A_{t_i} or n_{t_i}.[9] Thus the rate of nonradiative transitions

[9] One could take the derivative at different T, but this would complicate the discussion because the state of excitation changes during the application of ir.

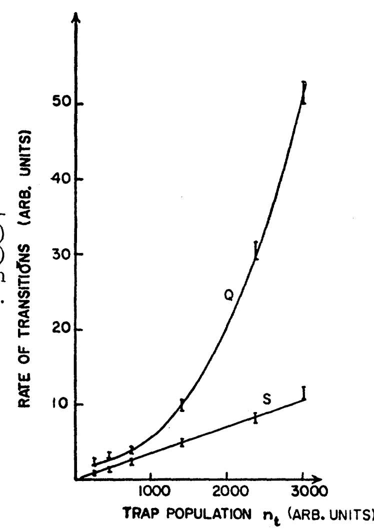

FIG. 2. Rate of s-ir-induced radiative (S) and nonradiative (Q) transitions, as function of trap population. *MS* 17.

Q induced by s-ir at certain trap populations n_{t_i} is found experimentally. This function $Q(n_{t_i})$ at the beginning of s-ir action is given in Fig. 2 and it is a good approach to a parabola. The errors chiefly arise from the subtraction in (1) and from taking the derivative. It may be emphasized again that each value of Q is obtained by a whole series of measurements of N_{nr} for various stimulation periods.

By a similar procedure the dependence of the rate of s-ir-induced radiative transitions upon the trap population n_{t_i} is obtained. Excitation is applied for a period t_i and phosphorescence observed for a period T. The area under the phosphorescence curve is called A_{ph}. The expression $A_{\text{stim}}-A_{\text{ph}}$ gives the number of radiative transitions integrated over T (A_{stim} was previously measured for the same period T when finding Q).

$$\int_0^T Sdt=A_{\text{stim}}-A_{\text{ph}}. \qquad (2)$$

Here S is the rate of radiative transitions induced by s-ir. This is done for different periods T and the integral in (2) is plotted as a function of T. The derivative of this function at $T\to 0$ gives S at the instant when the excitation ceases, and for the specific trap-population n_{t_i}. S is given in Fig. 2 as a function of n_{t_i}. It is a straight line. Thus

$$Q\propto n_t^2, \qquad (3)$$

$$S\propto n_t. \qquad (4)$$

In discussing the physical meaning of (3) and (4) it must be remembered that, because of charge neutrality,

$$n_t\approx p_t \qquad (5)$$

(p_t=number of trapped holes), because the number of free electrons n and holes p is small compared to the localized charges n_t and p_t. Inserting (5) in (3) gives

$Q \propto n_t p_t$. Assuming that after an excitation period t_i equilibrium exists between trapped holes in activators and free holes in the valence band, one can write $p_t \propto p$, and therefore $Q \propto n_t p$. This form, and therefore the experimental result (3), strongly supports the idea that the net quenching is a nonradiative recombination between free electrons and holes.

The difference between curves A_{II} and B_{II} (Fig. 1), mentioned above, comes from the fact that the amount of quenching which accompanies s-ir stimulation is different for different trap populations, while l-ir stimulation is not accompanied by quenching at low temperature. It can be seen from Fig. 2 that s-ir stimulation at low excitation is of the same order of magnitude as quenching, whereas the latter at full excitation is almost a factor of 10 higher than stimulation. This means that the stimulation peaks represented by curve A_{II}, Fig. 1 at low excitation (large missing glow area), are almost unaffected by the quenching superimposed onto stimulation, whereas at full excitation (small missing glow area) the peaks are diminished by almost a factor of 10. The stimulation peaks corrected to zero quenching are represented as a function of the missing glow area by the normalized curve A_{II}'. After this normalization both l-ir and s-ir stimulation decrease by about a factor of 100 in going from full excitation to that state of excitation in which only the shallow traps are empty (curves B_{II} and A_{II}'). Therefore to a first approximation, it can be assumed that strong stimulation only appears when the shallow traps are populated. This seems to contradict the results shown in curve S of Fig. 2, or Eq. (4), in which S increases linearly with total trap population. This however is no real contradiction, as shown below.

If ir stimulation were due to a release of electrons from traps and their subsequent recombination with activators, a dependence of S upon $n_t p_t$ would be expected. This dependence however is not found. This can be understood with the following assumption: The effect of infrared is to shift holes from certain ionized activator levels to other levels which have a higher recombination probability than those originally occupied. If this were correct, the stimulation rate S would increase proportionally to $p_t n$. As soon as the shallow traps are occupied, n, the number of conduction electrons, does not change very much anymore as mentioned above. To a first approximation, n can be considered constant as soon as a large percentage of shallow traps are filled, say above 75% or $n_t = 600$. Therefore, above this region, S should only depend on p_t or n_t (the total number of trapped charges). At very low population densities one should find deviation from linearity, because n is increasing as well as p_t, but in this region the total amount of stimulation is not easily determined. The linear increase of S is another indirect support of the finding that stimulation can occur only when shallow traps are filled and that when they are filled, the amount of stimulation only depends on the number of ionized

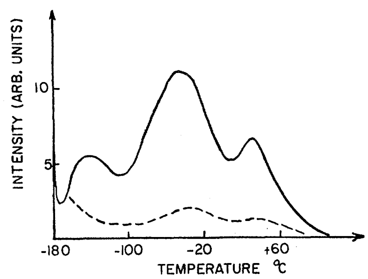

FIG. 3. Glow curve of MS 17 and height of l-ir-induced stimulation peaks (broken line).

activators available. This model not only explains the described properties of stimulation but also accounts for those found for quenching: Some of these ionized, more efficient activators may lose their charges thermally to the valence band, and these delocalized holes may recombine nonradiatively with trapped electrons [see Eq. (3)]. The equivalence of stimulation and quenching spectra strongly supports this.

The effects of ir on glow and photoconductivity give further direct evidence for a faster recombination rate caused by ir. If the suggested model is valid, stimulation peaks obtained during the glow should occur even after the shallowest traps have been emptied because conduction electrons are provided thermally from deeper traps. Under continuous infrared irradiation during the glow, a shift of the glow maxima to lower temperatures would be expected since the model predicts a faster recombination rate under ir.

C. Infrared-Induced Transitions During Glow

If during the measurement of a glow curve, short pulses of ir are applied to the sample, the emission rises after the l-ir is switched on, goes through a maximum, and decreases again. The l-ir is turned off after this maximum is reached. If this is done approximately every two minutes, an ordinary glow curve is obtained with stimulation peaks superimposed on it. Pulses of l-ir are used so that the long-time kinetics of the glow curve is not disturbed too much. In Fig. 3 the regular glow curve is shown as a solid curve. Only the heights of the stimulation peaks which actually appear atop the glow curve are given by the dashed curve. It can be seen that except for the first peak the height of the stimulation peaks is proportional to the glow intensity and not to the number of trapped electrons. This is another strong indication that ir does not act directly on trapped electrons. As seen in Fig. 1, the stimulation peak at liquid nitrogen temperature disappears as soon as the first glow peak is gone. During the glow curve however, stimulation is observed even in the later parts of the glow, after the shallow trapped electrons have disappeared or have certainly been greatly reduced in number. Since the rate, I, of radiative recombinations during the glow curve can be described by $I \propto p_t n$, and since the stimulation peaks are roughly proportional to the glow intensity as shown by Fig. 3, the rate of ir-induced radiative transitions S can also be described by the formula $S \propto p_t n$. This is in agreement with the results of Sec. B, which proposes that $S \propto p_t$ during excitation when n is almost constant. (n cannot be considered constant during the glow.)

The glow curve may also be investigated under continuous ir irradiation. At higher temperatures however l-ir begins to cause quenching as well as stimulation. This makes an interpretation of the glow curve more difficult.

D. Investigation of a Highly Stimulable Phosphor

This last type of experiment was however very successful with a ZnS(CuPb) phosphor (2150), which is highly stimulable and does exhibit less quenching than *MS* 17. The experiments performed are similar to those performed on *MS* 17 and the results are shown in Fig. 4. Curve A is the regular glow curve. The dotted curves E and D represent experiments similar to those in Fig. 1, method II. The ordinates of E and D are the height of the stimulation peaks obtained at liquid nitrogen temperature under s-ir and l-ir respectively. The abscissa for curves E and D gives the temperature to which the fully excited sample was heated before it was recooled and the stimulation peak measured. As soon as the first and second glow peaks were heated out, both l-ir and s-ir stimulation at low temperatures disappear. Considerable stimulation peaks were obtained during the glow. These are given by the broken curve F (Fig. 4) which shows the height of the stimulation peaks (reduced by a factor of 20) obtained at each point along the glow curve. It is similar to the analogous curve of Fig. 3, obtained from phosphor *MS* 17.

Curve B shows the glow curve under continuous l-ir irradiation. In order to compare glow curves A and B it is necessary to correlate the maximum in curve B, which occurs at about −85°C, to one of the maxima in curve A. This may possibly be done by determining the corresponding energy level using the method of varying the heating rate given by Schön.[10] As the heating rate is changed from q_1 to q_2, the position of the maximum shifts from T_1 to T_2. The corresponding energy level is given by

$$E=\frac{kT_1T_2}{T_1-T_2}\ln\left[\frac{q_1}{q_2}\left(\frac{T_2}{T_1}\right)^{7/2}\right]. \tag{7}$$

If this is done for the glow curve with continuous l-ir irradiation, and then for the glow curve without ir, $E_{\rm ir}=0.27$ ev is obtained for the maximum of curve B, which appears in Fig. 4 at −85°C, and $E_{\rm no\ ir}=0.25$ ev for the middle maximum of curve A which appears at about −45°C. Because of the similarity in energy levels of these two maxima, they may be correlated to each other, and it may be assumed that the middle maximum

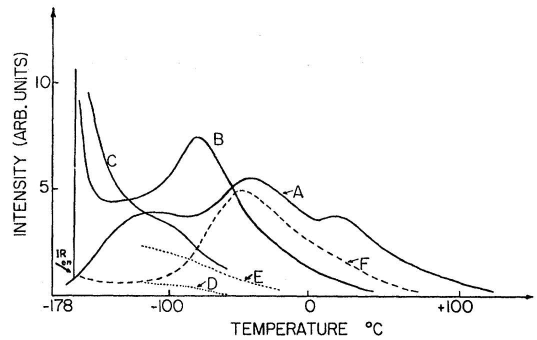

FIG. 4. Glow curves and stimulation peaks of 2150. A: Normal glow curve; B: under continuous l-ir; C: under continuous s-ir; F: l-ir-induced stimulation peaks (reduced twenty fold).

of curve A is shifted towards lower temperatures by ir irradiation. All glow curves represented in Fig. 4 are measured with the same heating rate. The last maximum in A does not appear in B, since even with phosphor 2150, l-ir produces quenching above 0°C. The first maximum in A does not appear in B because the shallowest traps are emptied by the large drain on conduction electrons, before the temperature rises sufficiently.

E. Evaluation of the Infrared-Induced Increase in Recombination Rate

It has been shown above that ir does not act directly on trapped electrons, thereby increasing the number of free electrons, but rather leads to an increased rate of recombination. This increased rate of recombination can be described by an increase of the coefficient β of recombination defined by $I=\beta n p_t$, where I denotes the instantaneous glow intensity. For the glow intensity under ir action, $I_{+\rm ir}=\beta_{+\rm ir} n p_t$. The ratio $\beta_{+\rm ir}/\beta$ can be determined using the theory of glow curves developed by Schön[10] in which T is the temperature of the respective glow maximum, q the heating rate, n_{t0} the trap population at the beginning of the glow, H the number of available traps, and $S_n \propto T^{\frac{7}{2}}\exp(-E/kT)$.

$$q(E/kT^2)=\beta(n_{t0}/H)S_n. \tag{7a}$$

The same equation can be used when the values of β, T, and s_n are changed by ir. Using the subscript $+$ir for these values under ir irradiation, equation (7a) becomes

$$q(E/kT_{+\rm ir}{}^2)=\beta_{+\rm ir}(n_{t0}/H)s_{n+\rm ir}. \tag{7b}$$

Dividing (7a) by (7b) yields

$$\frac{\beta_{+\rm ir}}{\beta}=\left(\frac{T}{T_{+\rm ir}}\right)^{7/2}\exp\left(-\frac{E}{k}\frac{T_{+\rm ir}-T}{T_{+\rm ir}T}\right). \tag{8}$$

This ratio is independent both of the heating rate and of the number of traps because these are not changed by ir. Inserting E determined from (7) and the glow

[10] M. Schön, Tech. Wiss. Abhandl. Osram-Ges. 7, 175 (1958).

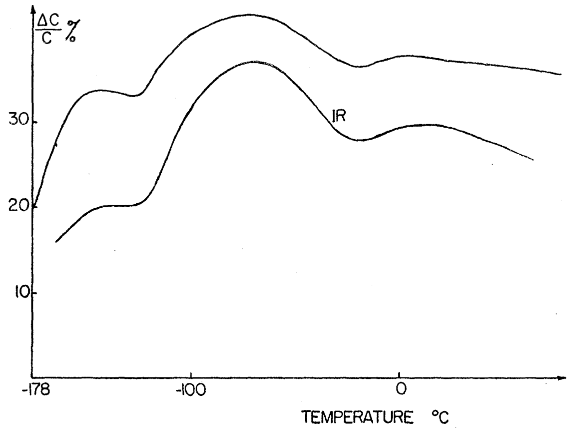

FIG. 5. Relative capacitance change of *MS* 17 during glow curve with and without l-ir application.

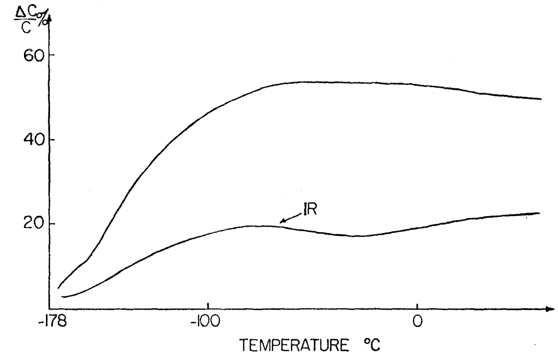

FIG. 6. Relative capacitance change of 2150 during glow curve with and without l-ir application.

peak temperatures of the two cases, it is found from (8) that $\beta_{+\mathrm{ir}}/\beta=15.0$ for the pair of glow curves (A and B) depicted in Fig. 4 (heating rate q_1). When the second pair of glow curves (heating rate q_2) is used to find $\beta_{+\mathrm{ir}}/\beta$, a value of 14.5 is obtained. This is in good agreement with the first value.

The increase of β under the action of ir can also be measured directly by applying l-ir when the middle maximum occurs in glow curve (A). This should increase the intensity by a factor of about 15. This is indeed the case. The broken line in Fig. 4 shows the increase of the glow intensity when l-ir is applied; it is found to be 16.5.[11]

If l-ir is applied during excitation at low temperature after the excitation time giving the glow curves shown, the intensity increases by a factor of 2.2. Since this factor is much smaller than 15 it must be assumed that the value of β is larger during excitation than during the middle of the glow curve. Using the model of the more efficient activator term, this means that a number of these more efficient activators must be ionized during excitation and therefore the additional effect of ir is not as large as during the glow. During the glow however, the more efficient activators disappear first and ir is required to produce them again and thus bring about a large enhancement. In the beginning of the glow curve (around the first maximum) however, some of the more efficient activators still remain ionized from the preceding excitation, so that the effect of ir pulses cannot be as large as in the later part of the glow. (See the broken curve in Fig. 3 and curve F in Fig. 4.)

If s-ir, which simultaneously causes stimulation and quenching, is continuously applied, glow curve C is obtained. The maximum is shifted to a lower temperature and appears only as a shoulder because quenching becomes prevalent at higher temperatures when s-ir is used.

[11] The stimulation peaks of phosphor *MS* 17 during glow (Fig. 3) show $\beta_{+\mathrm{ir}}/\beta=1.2$. This small increase of β produced by ir is not sufficient to produce a measurable shift in the glow peak under continuous ir as with 2150.

F. Comparison with Conductivity

From the hypothesis described above it would be expected that stimulation be accompanied by a decrease of conductivity, since ir stimulation makes conduction electrons disappear more rapidly (see Appendix B). The opposite (increased conductivity) should be observed if ir directly released electrons from traps (see Appendix A). The latter is not the case, as is shown by the following experiments.

Figures 5 and 6 present the results of the electric analogs of glow measurements of phosphors *MS* 17 and 2150 using the method of Kallmann *et al.*[12] The values of the relative capacitance change $\Delta C/C$, a measure of conductivity, are used. For *MS* 17 (Fig. 5) the conductivity decreases under pulsed l-ir, and decreases even more under continuous l-ir. The conductivity of 2150 also decreases under l-ir action (Fig. 6), and the maximum (which does not appear clearly, because the dark conductivity also rises) is shifted to lower temperatures, as previously seen in the luminescence measurements. These results confirm the idea that ir decreases the number of free electrons by producing a faster recombination rate.

SUMMARY

ir stimulation at low temperature only occurs as long as shallow traps are occupied, but its rate is proportional to the total number of filled traps or available ionized activators. As the temperature is raised, stimulation also occurs when only deep traps are occupied. This together with the observations that stimulation occurs at room temperature, that the wavelength dependence of ir stimulation and quenching are the same, and that stimulation often does not set in instantaneously when ir is applied, leads to the conclusion that the effect of ir is not a direct freeing of electrons from traps but rather a shifting of holes from activator levels of a smaller to

[12] H. Kallmann, B. Kramer, and A. Perlmutter, Phys. Rev. **89**, 700 (1953).

those of a larger recombination rate. This assumption accounts for all the observed results.

Photoconductivity measurements, which show that ir irradiation during the glow decreases the conductivity, are in agreement with this assumption. For a strongly stimulable phosphor these effects are very pronounced. The ratio of recombination rates for the two activator levels is about 15.

ACKNOWLEDGMENT

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APPENDIX

The luminescence intensity I, described as a bimolecular recombination between free electrons and ionized activators, is

$$I=\beta n p_t,$$

(β= recombination coefficient, n= concentration of conduction electrons, p_t= concentration of ionized activators, and n_t= concentration of trapped electrons). Under activator-band excitation at low temperature (no free holes), one has $p_t \approx n_t$ after reaching equilibrium ($n \ll n_t$), and therefore

$$I=\beta n n_t. \tag{A1}$$

A. Release of Electrons from Traps by Infrared

Assume that ir of wavelength 13 000 A releases trapped electrons directly during activator-band excitation. This ir radiation causes the following effects in the steady state at low temperature. Light intensity is unchanged (or slightly increased), conductivity is decreased. Giving I, n, and n_t the subscript ir for the case when ir is applied:

primary assumption; $n_{t\text{ir}} < n_t$, (A2)

from photoconductivity; $n_{\text{ir}} < n$, (A3)

from luminescence; $I_{\text{ir}} \approx I$. (A4)

Equation (A1) becomes

$$I_{\text{ir}}=\beta n_{\text{ir}} n_{t\text{ir}}, \tag{A5}$$

since there are still no free holes (no quenching and therefore $p_{t\text{ir}}=n_{t\text{ir}}$). Since the primary assumption is expressed by (A2), the comparison of (A1) and (A5) under the condition of (A4) would require $n_{\text{ir}}>n$. All experimental evidence is against this increase in the steady-state conductivity under ir irradiation. Therefore the assumption of a direct release of trapped electrons by ir is wrong.

B. Increase of β by Infrared Action

Assume that ir shifts electrons from activators with smaller to those with larger β. Then

$$I_{\text{ir}}=\beta_{\text{ir}} n_{\text{ir}} n_{t\text{ir}}.$$

Since $I_{\text{ir}} \approx I$, and since it is assumed that $\beta_{\text{ir}}>\beta$, it becomes

$$n_{\text{ir}} n_{t\text{ir}} < n n_t. \tag{A6}$$

In the equilibrium state not too close to saturation, from the thermal equilibrium

$$n_t/n=\text{const}=n_{t\text{ir}}/n_{\text{ir}}, \tag{A7}$$

or

$$n n_{t\text{ir}}=n_{\text{ir}} n_t. \tag{A8}$$

Dividing (A6) by (A8), one gets

$$n_{\text{ir}}<n,$$

which is found experimentally, and from the condition of thermal equilibrium (A7),

$$n_{t\text{ir}}<n_t.$$

Thus under the assumption of an increase in β produced by ir, the number of conduction electrons is decreased, which corresponds to the known decrease of the conductivity. Trapped electrons are released only indirectly via the thermal equilibrium between traps and conduction band. From this point of view it also becomes clear that no stimulation is observed at low temperature as soon as the shallowest traps are emptied because n decreases strongly at this point. It also becomes clear why a considerable delay of stimulation has been observed after a long dark period: At room temperature electrons can escape only very slowly from the deepest traps left filled after a long decay at room temperature.