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Infrared Stimulation and Quenching of Photoconductivity in Luminescent Powders*†

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Ac measurements of impedance changes in (ZnCd)S fluorescent powders upon addition of infrared radiation (a) simultaneously with the exciting ultraviolet and (b) various periods after excitation by ultraviolet or gamma radiation are described. A decrease (quenching) of conductivity is always observed in the steady state (a), but in case (b) a strong increase (stimulation) is often observed. The simultaneous quenching shows two maxima, one in the 7500 A region, the other about 12 500 A, but the stimulation decreases monotonically with increasing wavelengths. These two effects (quenching and stimulation) are superimposed; quenching can most easily be observed at relatively high conduction electron density, while stimulation is most easily observed long after excitation has ceased. The conductivity stimulation can be observed with most (ZnCd)S phosphors many days after cessation of excitation; thus these materials act as storage phosphors in which, however, the storage properties are observed by conductivity stimulation. Their light stimulability is often small. A specially activated Fonda-type storage phosphor with a very high light stimulability, however, shows only small conductivity stimulation. An explanation of this behavior and the wavelength dependence of the stimulation and quenching in terms of the action of infrared irradiation on trapped and valence-band electrons is given.

INTRODUCTION

THE change in conductivity of (ZnCd)S phosphors during and after excitation by light or high energy radiation has been investigated by means of dc and ac measurements.[1,2] The change of impedance observed in ac measurements was shown to be due to the increase in conductivity (more electrons in the conductivity band) of the phosphor rather than an increase in dielectric constant due to highly polarizable filled traps.[3] A simple model of conducting and nonconducting layers (the latter due to air spaces between separate grains, and between the electrodes and the sample) explains the main features of the capacitance saturation and shape of the Q-value curve.[2,4,5] In addition, the fact that the application of infrared light after excitation temporarily increased the capacitance change indicated even more conclusively that the impedance changes stemmed from changes in the conduction electron density rather than changes in the number of occupied traps.

It is well known that if infrared radiation is applied simultaneously with the exciting radiation, a quenching is observed in both the fluorescence and dc photoconductivity. Such quenching has been explained on the basis of the infrared light producing new possibilities of transitions of excited electrons to the ground states. However, the fact that some phosphors show first an increase in conductivity or light emission or both indicates that there is also an increased probability of transitions from traps to the conduction band.

After special activation, some (ZnCd)S phosphors display an increase in light emission due to infrared irradiations which may be observed many days after excitation has ceased (storage phosphors). A corresponding stimulation of conductivity has not been previously investigated, but should be expected if some electrons enter the conduction band when expelled from traps.

It should be noted that since some electrons may leave traps and recombine with the positive charges without emitting light, glow curves may not be a completely valid way of detecting traps. However, it is possible that such traps may empty into the conductivity band under infrared irradiation and thus will be detected by ac conductivity measurements (dc measurements are far less sensitive than ac measurements because of the existence of blocking layers). All traps, whether leading to radiative or nonradiative transitions can be also detected by the so-called "rise time" curves for photoconductivity and for light emission, since steady photoconductivity or light emission sets in only when all traps are filled to their equilibrium values. Such measurements, which will be reported in a later paper, show that practically all (ZnCd)S phosphors have deep traps whose number (for all substances) are of the same order of magnitude so that obviously a lack

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[1] H. Kallmann and B. Kramer, Phys. Rev. **87**, 91 (1952); see also E. A. Taft and M. H. Hebb, J. Opt. Soc. Am. **42**, 249 (1952).

[2] Kallmann, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953); for a general review article on this subject see J. Roux, J. phys. radium **15**, 176 (1954).

[3] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) **A188**, 485 (1947).

[4] C. G. Koops, Phys. Rev. **83**, 121 (1951).

[5] M. Borisov, Isvest. Bulgar. Akad. Nauk. **2**, 281 (1951).

TABLE I. Characteristics of phosphors investigated.

Powder	Composition	Color	Light[a] persistence After 1 min	Light[a] persistence After 5 min	Conductivity quenching (Simultaneous ultraviolet and infrared) Short wave-length A	Short wave-length $\delta C/C_0$, %	Long wave-length A	Long wave-length $\delta C/C_0$, %	Relative[b] light stimulability	Relative[c] current stimulability
Powder *A*[d]	ZnS(Cu)	Green	1.2×10^4	1.9×10^3	8500	4.5	12 500	3	5×10^5	100
LG-2150[e]	ZnS(Cu, Pb)	Green	3.5×10^5	2.9×10^4	6500	35	12 000	8	5×10^6	Negligible
Powder *O*	(ZnCd)S(Cu)	Orange	1.2×10^3	90	7500	6	12 000	1	1.6×10^4	100
Powder *N*	ZnS(Ag)	Blue	5.1×10^3	7.3×10^2	7000	1	12 500	0.7	1.8×10^3	3
Powder *R*[f]	ZnS(Cu)	Green	1.1×10^6	7.4×10^4	6500	12	12 000	2	7×10^4	1000
Powder *B*[d]	ZnS(Ag)	Blue	1.7×10^3	50	7000	1.5	12 500	1	1.7×10^5	100
Powder *M*[f]	ZnS(Cu)	Green	1.5×10^6	1.9×10^5	7000	2	12 500	1	3.8×10^4	10
Powder *K*	(ZnCd)S(Cu)	Yellow	5	2.5	7500	4	12 000	2	2.8×10^3	Negligible

[a] Arbitrary units; initial fluorescence about 150×10^6.
[b] Arbitrary units; 1 hour after ultraviolet excitation to trap saturation; 7–69 filter for infrared stimulation.
[c] Arbitrary units; 7–69 filter for infrared stimulation; values given are very approximate, since the exact determined ΔC peak cannot accurately be converted to induced conductivity.
[d] Supplied by the courtesy of Philips, Eindhoven; glow curve indicates only shallow traps [H. A. Klasens, J. Electrochem. Soc. **100**, 172 (1953); W. Hoogenstraaten, J. Electrochem. Soc. **100**, 356 (1953)].
[e] Manufactured by New Jersey Zinc Company.
[f] Powder *R* has Cu concentration of 0.007 percent; Powder *M* has Cu concentration of 0.004 percent.

of light or current stimulation is due to other causes than a mere lack of deep traps.

The measurements to be described in this paper are a continuation of the ac measurements previously discussed,[2] but in which the effect of application of infrared irradiation simultaneously with excitation, or during the decay period is more thoroughly investigated. It will be shown that almost all (ZnCd)S phosphors (even those with no light stimulation) contain deep traps which, when emptied, increase the conductivity of the powder sample, and that their photoconductivity is stimulable by infrared light days after excitation even without special activation. In addition, it will be shown that the infrared wavelengths most suitable for light stimulation in storage phosphors are also very important in photoconductivity, but that there is no direct correlation between current and light stimulation.

It will be recalled[2] that an increase in conductivity results in an increase in the measured capacity of the powder sample up to the point where the saturation value of the capacitance is reached. The *Q*-curve, on the other hand, goes through a minimum with increasing excitation, and is steep only at low or high intensities. Thus, for most cases, the change in measured capacity will be used as an indication of the conductivity; however, at low intensities where the capacitance curve is flat or at high intensities where the capacitance curve is close to saturation, the *Q*-values are more sensitive to conductivity changes.

The experimental results will be described in two parts; the first dealing with the effects obtained with simultaneous application of infrared irradiation (steady state), the second dealing with the effects obtained when infrared is applied after excitation.

The powders investigated were chosen to represent a wide range of characteristics as far as composition, activators, and light persistence and stimulation are concerned (see Table I).

2. EXPERIMENTAL RESULTS

A. Apparatus

The impedance measurements described were obtained with a General Radio 716-C Bridge (Schering type) with an oscilloscope used as a detector.[6] The powder samples were made using a small amount of Duco cement as a binder, the areal density ranging between 5 and 25 milligrams/cm². The electrodes were Nesa glass on one side and a flexible aluminum foil under pressure on the other side. With foils of several cm² in area, dark capacitance values up to 100 micromicrofarads were obtained. (The foils must be pressed strongly against the powder, otherwise a thin air layer adjacent to the electrode may diminish the capacity in an uncontrolled way.)

The excitation was provided by either a Mineralight or Hanovia ultraviolet source filtered so that most radiation was around 3650 A. The actual intensity incident on the powder was about 10 microwatts.

Infrared irradiation was supplied either by a 250-watt tungsten source through suitable filters or with a

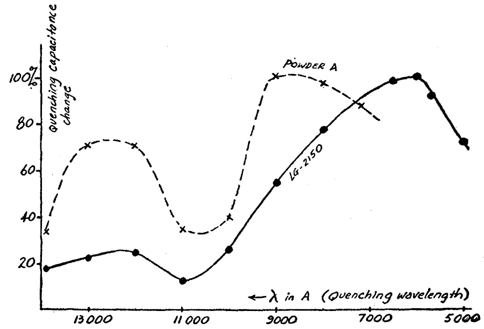

FIG. 1. Capacitance quenching (simultaneous ultraviolet and infrared) as a function of infrared wavelength for powders *A* and *LG*-2150. (Normalized.)

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[6] Measuring frequency 1000 cps or 10 000 cps.

Bausch & Lomb monochromator. The intensity of the former over the entire infrared region was about 10 milliwatts/cm^2; the latter was adjusted so that about 100 microwatts/cm^2 was obtained at any wavelength setting. The particular filters used with the tungsten source will be described below. The substances used are listed in Table I together with their electrical and optical characteristics.

The gamma source used in the experiments is a 1-millicurie radium source placed at an average distance of about 1 inch from the sample (1.3 r/hour).

B. Simultaneous Infrared Irradiation

All (ZnCd)S luminescent powders investigated display a quenching[7] of conductivity in the steady state under infrared irradiation (0.7 to 1.5 microns) added to existing ultraviolet excitation; that is, the capacitance decreases, and Q increases for low excitation intensities (left side of the Q-curve, Fig. 2 of reference 2). This quenching is also observed in the fluorescence and dc conductivity of all (ZnCd)S powders measured.

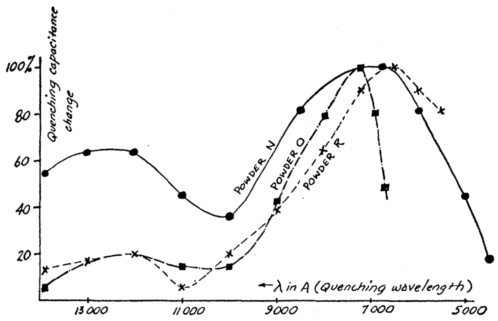

FIG. 2. Capacitance quenching (simultaneous ultraviolet and infrared) as a function of infrared wavelength for powders N, O, and R. (Normalized.)

Figures 1 and 2 show this quenching effect for five different samples. Table I also includes information on 3 additional powders. The quenching there is given in terms of the change of capacitance from ultraviolet to ultraviolet plus infrared excitation $\delta C = (C_{\mathrm{uv}} - C_{\mathrm{uv+ir}})$ divided by the dark capacitance (C_0); and the abscissa gives the wavelength of infrared irradiation. In the curves (Figs. 1, 2) the ordinates are given in percentage of the maximum quenching, which can be taken from Table I. It can be seen that for these substances there are two quenching maxima; one in the 12 500 A region; the other below 9000 A. Only powder A gives approximately equal quenching in both bands; the others show much stronger quenching at the shorter-wavelength region.

TABLE II. Correlation of capacitance change and intensity at about 0.1 microwatt/cm^2.

Phosphor	Percentage change for factor of 10 in intensity
Powder A	12
Powder LG-2150	8
Powder O	13
Powder N	10
Powder R	10

Since the capacitance for all these powders changes by 5 to 20 percent[8] when the intensity of excitation in the range used is changed by a factor of 10 (see Table II for actual percentage for each powder), these measurements show that the highest capacitance quenching (LG-2150) corresponds to a change in excitation greater than two orders of magnitude at the short-wavelength band, and by a factor of almost one order of magnitude at long wavelengths. All other samples show a quenching by a factor smaller than one order of magnitude at short wavelengths, with a smaller quenching at long wavelengths. All these infrared quenching measurements were carried out with constant ultraviolet excitation of about 0.1 microwatt/cm^2.

The quenching curve for powder A shows that a peak is reached at about 9000 A rather than about 7500 A as for most other substances. It will be shown below that this may be due to a simultaneous infrared-induced stimulation of conductivity that is particularly strong in the 7500 A region for this substance. This stimulation is always overridden by the quenching effect in the steady state with simultaneous excitation as will be discussed below. However, during the decay it shows up clearly immediately upon application and removal of infrared irradiation; as noted before, it also shows up as a temporary increase in conductivity during excitation before the over-all quenching sets in. It may be noted that the over-all shape of quenching *vs* wavelength curve (Figs. 1, 2) does not show much dependence either upon the Cd content, type of activator, or luminescent properties, except that the quenching drops

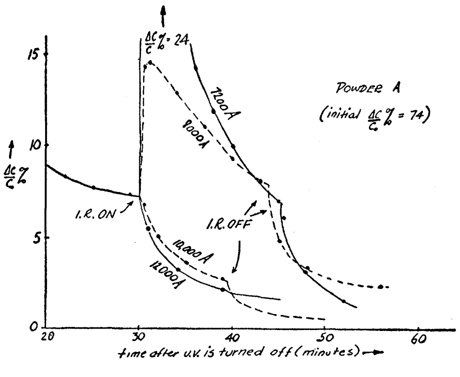

FIG. 3. Change in capacitance upon application of various infrared wavelengths after ultraviolet excitation for powder A.

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[7] There is also a temporary increase in conductivity immediately after infrared application; this is especially noticeable at low ultraviolet intensities and is due to a release of trapped electrons into the conductivity band or due to the creation of free holes in the valence band.

[8] For the general shape of capacitance *versus* intensity curves see reference 2.

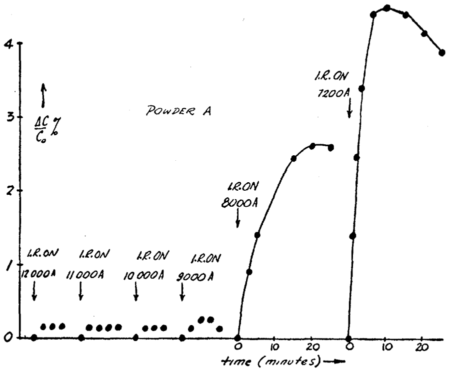

FIG. 4. Change in capacitance upon application of various infrared wavelengths three days after ultraviolet excitation for powder *A*.

off more steeply at the short wavelength end for (ZnCd)S powders, since they can already be excited in this wavelength region.

C. Infrared Irradiation after Excitation

Figure 3 shows the effect of infrared radiation of various wavelengths during the current decay of a powder *A* one-half hour after removal of 10 microwatts of ultraviolet excitation. Infrared at 7200 A and 8000 A shows a strong increase in capacitance (stimulation of conductivity) contrary to the quenching obtained with simultaneous ultraviolet excitation (Fig. 1); these changes of capacitance are described by $\Delta C = C_{\text{uv}} - C_0$. When the infrared light is turned off there is a sharp instantaneous drop in capacitance even below the normal decay curve. This is another indication of conductivity stimulation[7] and allows the detection of such stimulation even when the over-all effect is that of quenching. Using 10 000 A and 12 000 A infrared irradiation, a strong quenching of the decaying conductivity is observed. Although these wavelengths show a pronounced quenching, the instantaneous sharp drop when these wavelengths are turned off indicates some stimulation is occurring although it is almost negligible at 12 000 A.

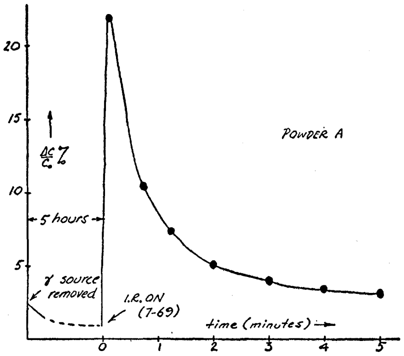

FIG. 5. Change in capacitance due to infrared irradiation five hours after gamma excitation for powder *A*.

A long-time stimulation (performed a long period of time after excitation) of this powder is shown in Fig. 4. The powder was excited by ultraviolet and, after a three-day period in the dark, was irradiated successively by infrared of 12 000, 11 000, 10 000, 9000, 8000 and 7200 A in that order. Down through 10 000 A there was very little stimulation (the small increase in capacity may be due to some stray light), but at 8000 A and 7200 A there is a marked increase of capacitance reflecting the increase of conductivity.

This experiment shows conclusively that the capacity changes noted in (ZnCd)S powders cannot be due to electrons while they are in traps since these curves show that the capacitance is increased when the traps are emptied, presumably into the conduction band.

These capacitance changes may be compared to the light emission obtained with storage phosphors when irradiated with infrared a long time after excitation; these changes of capacitance are due to a stimulation in conductivity and are thus not limited to the presence of a second activator which makes a luminescent material a good light stimulable phosphor. It will be shown that light stimulation does not necessarily require an increase of the density of electrons in the conductivity band; thus such a storage phosphor may not show current stimulation because the probability of recombination accompanied by light emission is so large that the lifetime of the electrons in the conductivity band may be quite short.

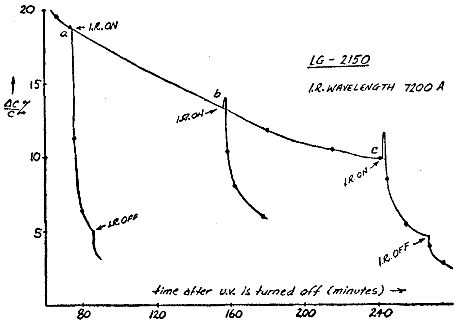

FIG. 6. Change in capacitance due to infrared irradiation during conductivity decay of Fonda phosphor *LG*-2150.

Powder *A* also shows a strong stimulation 5 hours after gamma irradiation (Fig. 5). After the capacitance change had decreased from 2.5 percent to 1 percent, a stimulation greater than 20 percent was observed when infrared irradiation was applied. The capacitance change rises to a peak of 20 percent at this time although the capacity change during excitation was only about 2.5 percent, indicating that the gamma excitation was utilized mainly in filling traps, rather than building up a large conduction-electron density. A 7-69 filter was used in this experiment; this passes a band of infrared between 7200 A and 10 000 A with an intensity of about 1 milliwatt/cm^2. Thus in the case of very weak excitation such as with high-energy radiation (the gamma excitation corresponded to an absorbed energy of only 4×10^{-11} watt/cm^2), radiation is much more easily detectable by stimulating the sample after a certain time of irradiation and observing its capacitance change than by measuring this change during excitation.

Figure 6 shows the effect of infrared irradiation during the decay of the conductivity of powder *LG*-2150, a strong light-stimulable phosphor. Although this particular powder is a Fonda-type[9] phosphor [ZnS(Cu,Pb)] and shows tremendous light stimulation, the over-all current stimulation is quite small (when observed) and a large quenching is obtained when infrared of 7200 A is applied. This is in agreement with the strong simultaneous infrared conductivity quenching for this powder. This strong quenching is presumably caused by recombinations accompanied by light emission which are very frequent in this substance (see conclusions). The current stimulation cannot be observed until after several hours of decay [points (b) and (c) of Fig. 6], earlier (a) only the quenching can be seen. However, after the infrared is removed, a further drop is observed, indicating that some current stimulation was occurring during the quenching. Another factor tending to decrease any current stimulation is the fact that this powder has an extremely slow rate of decay; that is, even after several hours the remaining conductivity is still large. Thus, the quenching effect (which is already large for this particular phosphor) is far more important than the stimulating effect. This highly light-stimulable substance is the one which shows the weakest current-stimulation, even when this long decay of conductivity is taken into account.

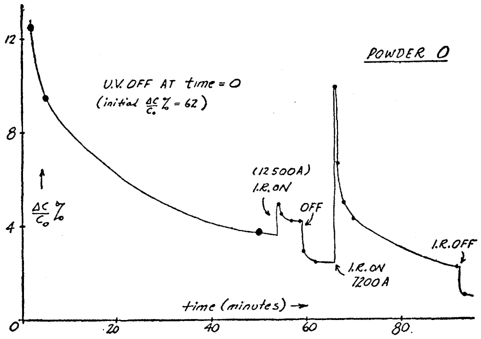

FIG. 7. Change in capacitance due to infrared irradiation during conductivity decay of powder *O*.

A decay curve starting with full (ultraviolet) excited sample shows a slow decrease similar to Fig. 6; 15 hours after excitation the application of infrared of 7200 A shows a stimulation, but much smaller than with powder *A*, then a quenching; radiation with 12 500 A, however, shows only quenching.

The effect of infrared irradiation on the conductivity of an orange-luminescent phosphor with very short light decay (powder *O*) is shown in Fig. 7. A much faster conductivity decay is observed (few shallow traps) than with the long decaying 2150 substance. About 1 hour after excitation, the application of 12 500 A infrared results in a small but noticeable capacitance increase (current stimulation). Following this, 7200 A infrared is applied, and a much stronger stimulation is observed. A still stronger stimulation is observed (Fig. 8) when the sample is left in the dark for 10 hours and irradiated using a 7-56 filter.[10] Thus, again, a long-time stimulable conductivity is observed, even with a short persistent, practically nonlight-stimulable (ZnCd)S phosphor.

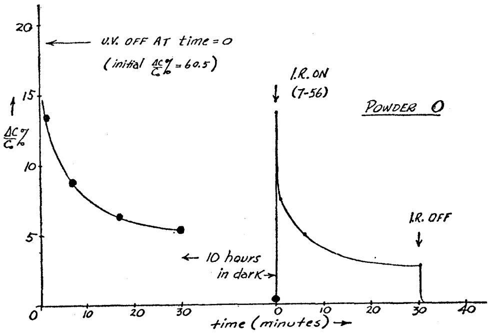

FIG. 8. Change in capacitance due to infrared irradiation 10 hours after ultraviolet excitation for powder *O*.

Previous gamma excitation also yields a stimulation of conductivity. About one-half hour after the gamma radiation has been removed, a strong current stimulation is observed with 7-56 infrared irradiation. All the traps were not emptied in the first infrared application; after 2.5 hours in the dark a second infrared application again resulted in a noticeable further stimulation.

Powder *N* is also a relatively fast-decaying powder, dropping from a capacitance change of 62 percent to 20 percent in less than 10 minutes, again indicating only a small density of shallow traps. Short-wave infrared irradiation (7-69 filter) shows a strong stimulation 20 hours after full ultraviolet excitation (Fig. 9) indicating a considerable number of deeper traps. If infrared irradiation of longer wavelength (7-56) is applied,

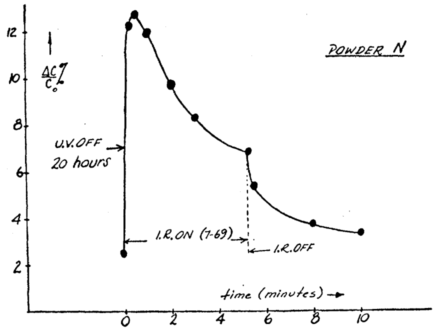

FIG. 9. Change in capacitance due to infrared irradiation 20 hours after ultraviolet excitation for powder *N*.

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[9] G. R. Fonda, Trans. Electrochem. Soc. **87**, 339 (1945).

[10] Passing wavelengths greater than 8000 A, intensity about 10 milliwatts/cm^2.

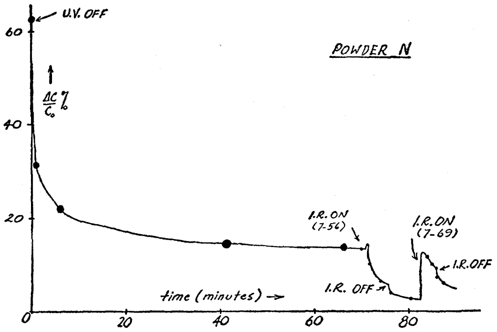

FIG. 10. Change in capacitance due to infrared irradiation during conductivity decay for powder *N*.

about 70 minutes after full ultraviolet excitation (Fig. 10), only a short stimulation pulse is noted followed by a pronounced quenching. If infrared is applied by using a 7-69 filter after application of the longer wavelength infrared, a stimulation peak similar to that of Figs. 9 and 11 is obtained. One hour after gamma excitation, stimulation by 7-69 infrared irradiation is also observable (capacity changes from 4 to 10 percent) with this powder (Fig. 11).

Powder *R* displays a very long light decay and weak stimulated light emission; its conductivity is also slow-decaying but shows strong stimulability. In Fig. 12 can be seen the very slow decay followed by the quenching when infrared of various wavelengths are applied 20 minutes after excitation has ceased. The wavelength showing the strongest quenching is 7200 A followed by 9000 A, 12 000 A, and 10 500 A, respectively, exactly as could be inferred from the simultaneous quenching curve (Fig. 2). It should be noted that the two short wavelengths show small stimulation peaks before quenching sets in; this stimulation can also be seen from the further drop in the decay of conductivity when these wavelengths are turned off. The long wavelengths, however, produce no noticeable stimulation although the quenching effect is weaker. The stimulation using 12 500 A twelve hours after full ultraviolet excitation is scarcely noticeable (about 0.25 percent capacity change) followed by a quenching of the same order of magnitude. When the infrared was turned off there was a further drop of 1 percent capacity change.

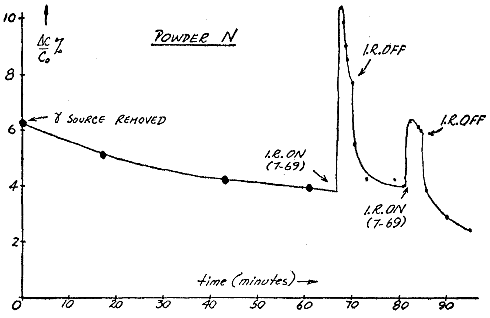

FIG. 11. Change in capacitance due to infrared irradiation after gamma excitation for powder *N*.

This powder however shows strong stimulation using 7200 A infrared irradiation about one hour after gamma excitation (Fig. 13). A tremendous increase in capacity is observed (25 percent) although the equilibrium capacitance change after 15 hours of gamma excitation is only 12 percent. The reason for the large stimulation peak in this run is due to the much smaller conductivity present immediately before stimulation (see Sec. 3).

Besides these substances, other phosphors have been investigated with similar results. These are given in Table I. It is seen that one of the two substances with weak current stimulation is 2150, which showed the highest stimulated light emission.

It may be noted that there is a definite similarity between the light decay curves and the capacity decay curves when the relation between $\Delta C/C_0$ and intensity of excitation is taken into account (Table II). Thus powders *LG*-2150 and *R* which show the longest light persistence also show the longest conductivity persistence, while powder *O* which has almost no light persistence shows an extremely fast current decay. After several minutes the conductivity of powder *R* has decreased to approximately one-tenth the initial value, while in the same time interval powder *O* has decreased to 10^{-5} of the initial value.

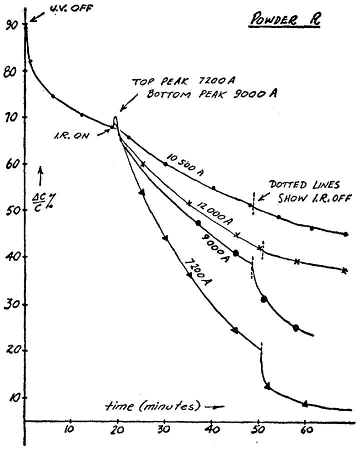

FIG. 12. Change in capacitance due to various infrared wavelengths during conductivity decay for powder *R*.

The increase in capacitance under infrared irradiation can be transformed to equivalent excitation intensity (Table II), and the stimulations observed can thus be compared with each other. This is done in the last column of Table I for stimulation after previous excitation. Thus the last two columns give an approximate comparison between light stimulability and current stimulability for the powders investigated. It is quite evident that the powder with the highest current stimulability has a relatively weak light stimulability, while the highest light-stimulable powder has one of the weakest current stimulabilities.

It should be mentioned that all the capacitance changes observed under illumination or stimulation can be duplicated by observing the dissipation factor or the Q-value instead. In this case, however, it must be considered that the Q-factor changes with increasing conductivity quite differently from the capacitance. With increasing conductivity it first drops sharply, goes through a minimum and rises again with increasing conductivity (see Fig. 4 of reference 2). Hence, with current stimulation, for instance, a decrease of Q is obtained if one works on the descending branch of the Q-curve, but an increase will result on the ascending branch of the Q-curve; with current quenching just the converse effects are obtained. Since it is not always possible to say in which part of the Q-curve the observations are performed, especially if fast changes in conductivity occur, it is more convenient to investigate the changes in C in order to gain information about the changes in conductivity. As an example, the corresponding changes of C and Q for a sample of powder O are described in Fig. 14 for excitation, decay, stimulation, and quenching. In the first 40 minutes the conductivity buildup is seen and the rise in C is accompanied by a drop in Q. When the exciting ultraviolet illumination is turned off (first broken line), C drops and Q rises but not quite to its original dark value. When infrared is turned on (second broken line), C abruptly jumps to a high value and Q drops just as fast; then C drops slowly again because of the decay of conductivity under infrared irradiation. Q, however, drops even further at the beginning because with this stimulation a point was reached which was on the right side of the Q-minimum. After passing this minimum, the Q-value rises since at low conductivity the Q values increase with decreasing conductivity.

3. CONCLUSIONS AND DISCUSSION

In general, the discussion of stimulation and quenching of light emission or conductivity in the (ZnCd)S phosphors by infrared radiation has involved the release of electrons from traps and the production of free holes in the valence band. On the basis of the above experiments it is possible to complement this mechanism.

First, it must be stressed that these experiments on conductivity stimulation and quenching show that different elementary processes are induced by the same infrared wavelengths. Quenching is most obviously observed in the steady state (simultaneous excitation and infrared irradiation). Here infrared irradiation decreases the light emission and also the conductivity over the whole range of infrared wavelengths with two maxima of quenching, around 12 500 A and 7000–8000 A. It must, however, be borne in mind that this observed decrease in conductivity is a superposition of a stimulation and a quenching process in which the quenching effect always prevails. This is noteworthy since it is not as evident as it is in the case of light emission. Without infrared irradiation, most excited electrons return to the ground state accompanied by light emission; hence additional infrared irradiation cannot increase the light emission in the steady state, since almost all excited electrons emit light in any case. Therefore, if infrared creates nonradiative transitions, the over-all effect must be that of light quenching, and this is correct even when some slight quenching also occurs under normal conditions without infrared.

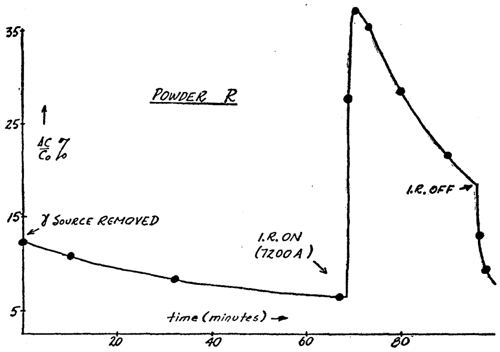

FIG. 13. Change in capacitance due to infrared irradiation after gamma excitation for powder R.

This is not necessarily the case with conductivity, which depends upon the density of electrons in the conduction band (and perhaps to a lesser degree on that of holes in the valence band). The density in the conduction band would be increased if infrared irradiation only releases additional electrons into this band from traps and would be decreased if infrared irradiation only produces new transitions to the valence band (recombination); the experiments show that both processes occur simultaneously and thus it is not evident which process will prevail. The experiments show that in the steady state the density of electrons in the conduction band is always decreased by infrared irradiation (at least at room temperature); this means that the

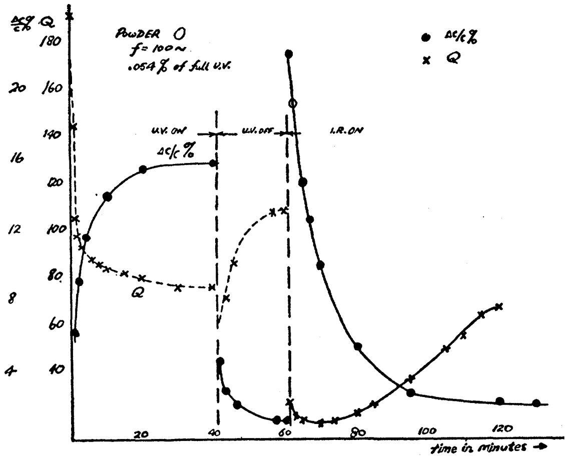

FIG. 14. Capacitance change and Q-curve for powder O showing excitation, decay, and infrared stimulation.

drain of electrons from this band by recombinations created by infrared irradiation surpasses the stimulation of electrons into the conductivity band.

Stimulation is more easily observed in the nonsteady state, along the decay curve of conductivity. Here the net effect also depends on the magnitude of both stimulation and quenching. Since the amount of quenching depends on the density of electrons already present in the conduction band before infrared is applied, the absolute amount of quenching is low when only a small conductivity (low-conduction density) is available to be quenched. But stimulation can then be easily observed since electrons are released from deep traps (filled by previous strong excitation) into the nearly empty conduction band. Thus at high-electron density in the conduction band (immediately after excitation) the net effect is often that of quenching or of only small stimulation, whereas further along the decay curve stimulation becomes more pronounced particularly for shorter infrared wavelength; at very low conductivity (very long after excitation) quenching obviously cannot be detected at all. These effects are similar to those observed with dc conductivity.[1]

It may be emphasized again that stimulation into the conduction band can still be observed even when the over-all effect is that of quenching along the decay curve. If, during the ac conductivity decay, the infrared radiation is turned off, a further instantaneous drop in conductivity occurs (see Fig. 6, for instance). This drop is caused by the sudden cessation of the electron transfer from traps into the conduction band due to infrared. The magnitude of this drop is thus also a measure of the stimulation by infrared.

It is found that stimulation decreases monotonically with increasing λ and practically vanishes in the region of 12 000 to 13 000 A. Thus, the wavelength dependence of current stimulation and of quenching seem to be quite different since the quenching displays two maxima, one in the region where stimulation has practically vanished.

The maxima of the quenching process can be observed, not only in the steady state (simultaneous excitation and infrared irradiation) but also along the decay curve. The drop in the decay curve due to infrared irradiation (see for instance Fig. 12—powder *R*) is stronger for 7200 A than for 9000 and 10 500 A but increases again for 12 000 A in complete agreement with the steady-state quenching curve of this substance (Fig. 2).

Light stimulation and quenching differ in behavior from that of the conductivity. The observed light quenching curves show similar maxima as the current quenching curve, indicating that both are in some way connected with each other, but when the influence of infrared on the light decay is studied, especially in the Fonda-type phosphors, strong light stimulation often occurs at the same wavelengths where current quenching prevails. Further, the light-stimulation curve is not monotonic but displays the same maxima as the quenching curve. Strong-light stimulation occurring a long time after excitation has ceased and due to special activation is relatively rare, whereas current stimulation of such a type occurs in many substances.

To explain these observations together with the known effects of light stimulation in Fonda-type phosphors,[11] it is assumed that the current stimulation is always due to the release of electrons from traps ranging down to approximately one volt (measured from the bottom of the conduction band); that traps of such depth are present in appreciable number follows from the fact that stimulation of conductivity (not the conductivity itself) decays only extremely slowly with time (three days after excitation considerable conductivity is still stimulated; Fig. 4). Before the addition of infrared, the number of trapped electrons are in equilibrium with the number in the conduction band (n_c) in accordance with the equation[1]

$$n_c/n_t = n_c/n_{0t} + \delta_t/\beta n_{0t},$$

where n_t is the number of electrons occupying the traps of kind t, n_{0t} is the total number of traps of kind t available (both per unit volume), β is the probability for trapping, assumed equal for all traps, and δ_t is the probability per unit time of release of electrons from traps. Such an equation holds separately for each trap level. The addition of infrared irradiation effectively increases the δ_t term, as if a higher temperature were applied. The effect, therefore, for $n_c \ll n_t$, is that a larger number of electrons is now transferred into the conduction band, and an increase in conductivity would occur if the infrared induced no additional recombinations.

The quenching of light[12] and conductivity by infrared has been ascribed to the production of free-moving holes (*E* in Fig. 15) in the valence band by lifting electrons out of the valence band into some higher energy level (perhaps an ionized activator). The holes thus created are free to move and recombine with free (*D*)

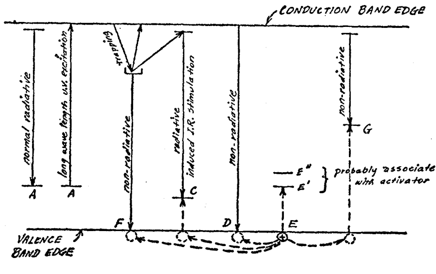

FIG. 15. Energy-level diagram for (ZnCd)S phosphors. *A* activators; *B* traps; *C* special activators (i.e., Pb); *D* radiationless recombination of hole and free electron; *E* hole; *F* radiationless recombination of trapped electron and hole; *G* radiationless recombination at quenching center.

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[11] See Fig. 15 for transitions discussed in the following paragraphs.

[12] M. Schon, Z. Physik **119**, 470 (1942); Ann. Physik **3**, 333 (1948).

or trapped (F) electrons directly or indirectly via centers (C, G), thus tending to decrease the density of conduction electrons. Light quenching, however, will only occur if some of these recombinations are nonradiative. It will be also assumed for the purpose of explaining the two quenching maxima, that there are at least two different energy levels involved in the production of holes (E', E'').

We attribute these two levels to the hole production process rather than to the release of electrons from traps because these maxima only occur in the current quenching and not in current stimulation. Besides this, there is evidence from investigation of light stimulation[13] indicating that these two maxima are not connected with different levels of trap. Of course, if this assumption is made, one must explain why two maxima occur in light stimulation and not in current stimulation. This will be done below.

The free holes moving in the valence band do not essentially contribute to conductivity since no indication of current stimulation is found for long wavelengths where a quenching maximum occurs. This may be due to the fact that the holes recombine quickly with the available electrons or are otherwise immediately retrapped.

In all (ZnCd)S phosphors tested up to now in this laboratory there was a definite quenching of the conductivity under additional infrared radiation (also noted in fluorescent light emission). This may be understood as follows. The electron density in the conductivity band at a certain ultraviolet intensity is mainly determined by the many shallow traps and not as much by the deep traps which are filled to saturation. From the shallow traps there is a constant release of electrons into the conduction band by thermal action (δ_t). Infrared irradiation increases this release, but not by a very large amount relative to this constantly present release by thermal action; the recombinations with the valence band, however, occur relatively seldom without infrared and are tremendously increased by such irradiation (as radiative or radiationless transitions) and the experiments show that this increase surpasses the increase in total release of electrons into the conductivity band.

The results obtained with light stimulation may be explained as follows. In the long-time light-stimulable substances (Fonda phosphor), two maxima in light stimulation occur corresponding to the quenching maxima of the light[9,14] and conductivity; the stimulability at the long infrared wavelength does not persist very long but decays considerably within one day.[15] To explain the coincidence of the light-stimulation maxima with those of conductivity-quenching maxima, it is assumed that at least two types of current-quenching centers exist; one which induces recombination accompanied by light emission (C), and the other which gives rise to radiationless transitions (D, F, and G). Both induce current quenching but only the second type causes light quenching. If the recombinations via the radiative centers are more probable (perhaps because of a larger recombination cross section) than the normal radiative transition via the activators and via the nonradiative centers, then light stimulation will be at its maximum when hole production is at a maximum and thus the quenching maxima and the light stimulation maxima will coincide in wavelength. The long wavelength light stimulation comes about by a recombination of electrons still in the conduction band or in shallow traps with the freed holes (via the aforementioned centers) whereas the shortwave maximum comes about by the simultaneous release of electrons from deep traps and of holes and their recombination thereafter. Thus in the case of special radiative centers, hole production induces light stimulation and strong current quenching since the probability of transitions to the ground state is augmented by the additional radiative centers. Thus it is found, particularly with light stimulable substances, that the net effect on conductivity (even at short wavelengths) is that of strong quenching soon after excitation; only at the later parts of the conductivity decay curve does stimulation become noticeable. However, in any case in such a substance the current stimulation is found to be weak since it is simultaneously counterbalanced by strong recombinations. In accordance with these ideas it was found that some substances with weak light stimulation show strong current stimulation.

The investigations reported in this paper show that the so-called storage phosphors are not as much distinguished by their storage properties as by their capability of light stimulation. The stimulation of conductivity long after excitation is very common and occurs in nearly all substances, indicating that many of them have equal storage qualities, but they differ tremendously in their capability of light emission when they are stimulated.

In this connection it may be noted that three methods of detecting electrons stored in deep traps have been discussed, namely the rise-time method, the infrared stimulation of light emission, and the infrared stimulation of conductivity. There is still another effect which can be used to detect such filled traps, the effect of persistent polarization in such photoconductive substances.[16] The persistence of this polarization depends on the time that electrons stay in these traps, and by measuring the decay of this polarization it is possible to obtain information about the number and depth of these traps.

In conclusion, it should be stressed that the given

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[13] (to be published).

[14] Polytechnic Institute of Brooklyn, Final Report for Contract NObsr 39045, June 30, 1949 (unpublished).

[15] (to be published).

[16] H. Kallmann and B. Rosenberg, Phys. Rev. **97**, 1596 (1955).

explanation may not be the only one that can be chosen to account for the stimulation and quenching with infrared radiation of conductivity and light in (ZnCd)S phosphors. Since it explains, with a minimum number of assumptions, the basic experimental results, and fits into the general band picture for these phosphors, it seems a reasonable starting point in a quantitative theory of the electronic transitions in such phosphors.

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Electrical Properties of *p*-Type Indium Antimonide at Low Temperatures*

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The electrical resistivity ρ, Hall coefficient R, and transverse magnetoresistive ratio $\Delta\rho/\rho$ of *p*-type single crystals of indium antimonide have been measured between 370°K and 1.5°K. Low-temperature anomalies similar to those observed by Hung on germanium have been found, a steep maximum in the $\log R$ *versus* $1/T$ curve and a change of slope of the $\log\rho$ *versus* $1/T$ curve. Contrary to the case with germanium, the magnetoresistive ratio of InSb does not vanish in the lowest temperature range, but it changes its sign from positive to negative as the sample is cooled to a temperature somewhat lower than that at which the Hall coefficient reaches its maximum value. Negative values of the magnetoresistive ratio cannot be explained by the usual theory of semiconductors. At the present time it also is not clear how Hung's model of impurity band conduction can account for negative values of the magnetoresistive ratio.

INTRODUCTION

AT temperatures above 78°K indium antimonide behaves like a conventional semiconductor, as previous measurements[1,2] of the Hall coefficient and the resistivity have shown.

Several materials, however, which show the normal behavior of semiconductors at higher temperatures exhibit anomalous electrical properties at low temperatures which cannot be explained by the usual semiconductor theory. Germanium, for instance, shows large deviations from the normal behavior in the range below 50°K, as Hung[3] discovered in 1950. The Hall coefficient of germanium does not increase indefinitely as the temperature is lowered, but reaches a maximum value and decreases thereafter by orders of magnitude. In the $\log\rho$ *vs* $1/T$ curve, one can distinguish a larger slope in the higher temperature range, before the Hall maximum is reached, and a much smaller slope at still lower temperatures.

Anomalies similar to those discovered by Hung on Ge have been found by Busch and Labhart[4] on SiC. Also, TiO_2 seems to show the same abnormal behavior at low temperatures, as recent measurements in this laboratory indicate.

As an explanation for the anomalous behavior of germanium at low temperatures, Hung[5] suggested that a small but finite conduction takes place in the impurity band, in addition to conduction in the ordinary conduction band.

A detailed theory of conduction in impurity bands has not yet been worked out. In any theoretical discussion, however, the explanation of the formation of a conducting impurity band with impurity concentrations as low as 10^{15}/cc is rather difficult. It would be of interest, therefore, to investigate whether other materials also exhibit anomalies at low temperatures and how they differ from those in germanium. This might throw some light on the conduction properties of impurity bands or even suggest a different explanation for the anomalies. For this reason, an investigation of the electrical properties of indium antimonide at very low temperatures has been undertaken.

This paper reports the measurements of electrical resistivity, Hall coefficient, and magnetoresistive ratio on several *p*-type single crystals of indium antimonide down to 2°K.[6]

EXPERIMENTAL PROCEDURE

A. Preparation of Samples

The samples used were prepared by Miss L. Roth of this laboratory. The indium obtained from the Indium

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* Supported by U. S. Signal Corps.

[1] H. Welker, Z. Naturforsch. **7a**, 744 (1952) and **8a**, 248 (1953), Physica **20**, 893 (1954), also Scientia Electr. **1**, 2 (1954); H. Weiss, Z. Naturforsch. **8a**, 463 (1953); R. G. Breckenridge, Phys. Rev. **90**, 488 (1953); M. Tanenbaum and J. P. Maita, Phys. Rev. **91**, 1009 (1953); Cunnel, Saker, and Edmond, Proc. Phys. Soc. (London) **B66**, 1115 (1953); O. Madelung and H. Weiss, Z. Naturforsch. **9a**, 527 (1954).

[2] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. **96**, 571 (1954).

[3] C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950) and **96**, 1226 (1954); see also H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).

[4] G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946).

[5] C. S. Hung, Phys. Rev. **79**, 727 (1950).

[6] Some low-temperature measurements on InSb have also been made by the Oxford group, without giving the details reported here. See J. Hatton and B. V. Rollin, Proc. Phys. Soc. (London) **A67**, 385 (1954).