

## Fluorescence and Phosphorescence of Thallium-Activated Potassium-Halide Phosphors

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### 1. COMPLEX THALLOUS IONS IN CONCENTRATED HALIDE SOLUTIONS

WHEN thallose chloride is dissolved in a concentrated aqueous solution of halides like KCl, NaCl, HCl, CaCl<sub>2</sub>, KBr, etc., new selective bands appear in the absorption spectra, with peaks at 2470Å for the chlorides and at 2650Å for the bromides, which do not occur in the pure halide solutions.<sup>1</sup> By absorption of light in these bands a fairly strong blue or blue-green fluorescence is excited in the chloride or bromide solution, respectively. A photometric measurement of the fluorescence intensity in a well-defined solution, for instance a 5-molar NaCl solution, affords the means for a quantitative determination of the Tl<sup>+</sup> concentration and thus provides a new method for quantitative analysis of Tl. At constant thallium concentration, e.g., 10<sup>-4</sup> molar, the fluorescence yield increases steadily with increasing Cl<sup>-</sup> concentration in a NaCl or CaCl<sub>2</sub> solution. However, for a KCl solution, which at room temperature is saturated at 3.9 molar, the increase of the fluorescence yield becomes much smaller when the KCl concentration is more than 2 molar. When the KCl solution is supersaturated, so that the salt begins to crystallize out, the solution loses its power of fluorescence almost completely. Simultaneously the selective bands in the absorption spectrum disappear. Quantitative fluorescence analysis shows that when 5 percent of the total quantity of KCl contained in a concentrated KCl solution has crystallized out by slow evap-

oration, not more than 1 percent of the thallium remains in the solution. If a weighed quantity of the crystals is redissolved in a nearly saturated KCl solution, a measurement of the fluorescence of this solution proves that the missing 99 percent of thallium is contained in the crystals. Similar results are obtained when the salt is not crystallized by slow evaporation, but is partially precipitated by addition of a quantity of HCl to the solution. Finally, the fluorescence of the KCl-Tl solution vanishes after some time if a number of solid KCl crystals are introduced into the solution, the process being accelerated by shaking. Solutions in which the potassium salt was replaced by a sodium or ammonium salt did not behave in the same way. After partial evaporation of a saturated NaCl solution containing 10<sup>-4</sup> molar Tl<sup>+</sup>, the Tl<sup>+</sup> concentration in the solution and the corresponding fluorescence intensity were not altered appreciably.

Solutions of KBr give quite analogous results. PbCl<sub>2</sub> in saturated KCl solutions also behaves very much like TlCl. By crystallization of a part of the potassium salt the lead is almost completely removed from the solution. Since the fluorescence is always rather weak in this case, the disappearance of the lead was proved by the stepwise disappearance of the selective band from the absorption spectrum. Similar observations were made by Otto Hahn and his collaborators<sup>2</sup> with regard to KCl solutions containing traces of radioactive lead. In this case also NaCl was much less effective than KCl in taking the lead out of the solution. It must be mentioned that these authors could not obtain the same effect with radioactive thallium isotopes. However, it seems to be not improbable that this discrepancy is due to the very short lifetimes of the Tl isotopes, which range from 3.1 min. for ThC'' to 4.76 sec. for AcC'', while among the lead isotopes ThB has a life of 10.6 hours and RaB a life of nearly 2 years.

\* Visiting professor at the University of Chicago. In *Physica* 7, 225 (1939) issued March, 1940, a paper was published by H. Vogels and myself, dealing with the fluorescence of complex ions of Tl, Pb, and Sn in concentrated aqueous halide solutions. Further work done in collaboration with Messrs. H. Vogels and E. Wasser was ready for publication at the time of the German invasion of Belgium. The manuscripts were lost. One part of the experiments was repeated during my stay at the University of California at Berkeley last year; for the other parts the numerical data are not available, but the qualitative results seem to be of sufficient interest to justify a short publication.

<sup>1</sup> H. Fromherz and Ku-Hu-Li, *Zeits. f. physik. Chemie* A153, 321 (1929).

<sup>2</sup> O. Hahn, H. Kaedig, and R. Mumubauer, *Zeits. f. Krist.* 87, 387 (1934).

## 2. FLUORESCENCE OF THE CRYSTALLIZED MATERIAL

The small crystals which are obtained by evaporation of a KCl or KBr solution containing traces of thalious ions are strongly fluorescent and phosphorescent even when still soaked with liquid solution. The luminescence becomes somewhat stronger by drying the crystals at a temperature of 40–50°C, but is not appreciably altered by heating to 250°C. The optical properties of these micro-crystalline powders are practically the same as those of the single crystal KCl-Tl and KBr-Tl phosphors as described by Pohl and his collaborators.<sup>3</sup> They have selective absorption bands *A* at 2475 and 2610Å, respectively, coinciding with the selective bands of the liquid solutions mentioned above, and a second short wave-length absorption band *C* at 1950 and 2000Å, respectively.<sup>4</sup> Absorption in these bands produces fluorescence. However, in contradistinction to the single crystal phosphors which have comparatively small Tl contents, in our phosphors the visible fluorescence is very strong.<sup>5</sup>

Since the first crystals deposited from the solution contain the largest fraction of the dissolved thallium, it is unfavorable to evaporate the whole solution for the preparation of strongly luminescent material. As soon as a small quantity of the salt has crystallized, the remaining solution must be decanted. In order to obtain crystals with a very high Tl content and a very

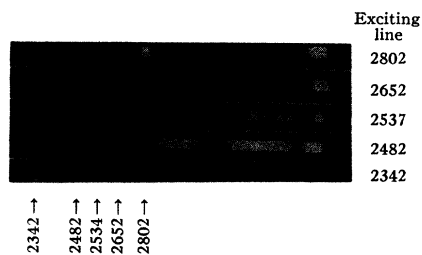


FIG. 1. Fluorescence spectra of a KCl, Tl phosphor excited by different mercury arc lines.

<sup>3</sup> R. Hilsch, Proc. Phys. Soc. **49**, extra part, p. 40 (1937).

<sup>4</sup> This second absorption band *C* is also found in the liquid solutions, but only the steep increase of absorption power below 2250 and 2400Å, respectively, has been observed, without attaining the peaks of the bands.

<sup>5</sup> The papers of Pohl's collaborators deal almost exclusively with the ultraviolet emission of alkali halide phosphors. Only in one paper by Buenger and Flexig is a visible (blue) emission band mentioned.

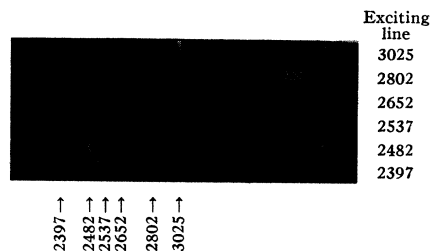


FIG. 2. Fluorescence spectra of a KBr, Tl phosphor excited by different mercury arc lines.

brilliant luminescence, an aqueous solution is saturated with KCl and TlCl at the boiling point, and as soon as by cooling a small fraction of the salt has crystallized the rest of the liquid is decanted. Thus crystals with a Tl content up to 3 percent can be obtained, as proved by the fluorescence analysis described above. The later crystal fractions become poorer and poorer in thallium; in the very last ones no fluorescence due to the presence of thallium can be excited.

Mere visual observation shows that not only the intensity but also the color of the fluorescence depends to a high degree on the thallium concentration in the crystals. With little thallium the fluorescence is blue violet, with increasing thallium concentration it turns into bluish green, and the crystals with the highest thallium content exhibit a brilliant yellowish white luminescence.

If the ultraviolet part of a mercury arc spectrum is focused upon a surface covered with a phosphor of the last kind, the fluorescence excited by adjacent mercury lines shows varying colors. Thus the fluorescence of the chloride phosphor is blue violet when excited by Hg 2537 and 2482Å, greenish yellow when excited by Hg 2652Å, and orange when excited by Hg 2399 or Hg 2802Å. In the case of the bromide phosphor the closely neighboring lines 2537 and 2482Å produce strikingly different fluorescence colors, the one being blue and the other yellow.

Spectrograms of the fluorescence excited by the isolated Hg lines prove that the fluorescence spectra of the KCl, Tl and KBr, Tl phosphors consist of three or even four independent bands (see Figs. 1 and 2) and that the relative intensities of these bands in the emission spectrum depend on the wave-length of the exciting light, as represented in Table I. The complete band spectrum with the ultraviolet band *a* prevailing is excited by those Hg lines alone which coincide

TABLE I. Relative intensities of emission bands. *s*, *m*, *w*=strong, medium, weak excitation by Hg line at top of column.

Phosphor	Exciting Hg lines: Emission band	2352	2399	2482	2537	2652	2753	2804	2894	3025	3126A
KCl-Tl	{ <i>a</i> 2800-3300 peak 3000	—	—	<i>s</i>	<i>s</i>	—	—	—	—	—	—
Absorption band <i>A</i>	<i>b</i> 3600-4050	—	—	<i>s</i>	<i>s</i>	?	—	—	—	—	—
peak 2475	<i>b'</i> 4300-5000	<i>w</i>	<i>m</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>w</i>	<i>w</i>	—	—	—
	<i>c</i> 5600-6000	<i>s</i>	<i>m</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—	—	—
KBr-Tl	{ <i>a</i> 3100-3600 peak 3250	—	—	—	<i>s</i>	<i>s</i>	—	<i>w</i>	—	—	—
Absorption band <i>A</i>	<i>b</i> 3400-4300	<i>s</i>	<i>s</i>	<i>m</i>	<i>s</i>	<i>s</i>	—	<i>s</i>	<i>s</i>	<i>m</i>	—
peak 2610	<i>c</i> 4200-6000	<i>m</i>	<i>s</i>	<i>s</i>	<i>m</i>	<i>m</i>	—	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>

nearly with the peak of absorption band *A*. The more the wave-length of the exciting light is shifted toward the long wave-length or the short wave-length edge of the absorption band *A*, the more the emission band *a* disappears and the visible emission bands prevail. The analogy in the behavior of the chloride and the bromide phosphor with regard to the Hg lines 4828 and 2537A in the first case and to the Hg lines 2537 and 2652A in the second case is clearly shown by Table I.

In phosphors of smaller thallium content the Hg lines of greatest wave-length mentioned in Table I are no longer able to excite fluorescence. Thus a bromide phosphor could be prepared, the fluorescence of which could not be stimulated by Hg 3126, while it emitted a yellow fluorescence under the action of Hg 3025. In another case this line was also inefficient, but yellow fluorescence was still excited by Hg 2802A. Finally in KBr-Tl phosphors with the smallest Tl concentration the Hg lines 2652 and 2537A alone produced a strong blue-green emission.

It seems therefore that the spectral region within which the phosphors are able to absorb light broadens toward greater and probably also towards shorter wave-lengths with increasing Tl concentration. It is not possible to decide whether this is due to a broadening of the band *A* which is characteristic of the single crystal phosphors of low Tl concentration, or to the appearance of new bands originating from spots of abnormally high Tl concentration. The latter assumption may be suggested by the fact that the fluorescence excited by light absorption in the new region of the absorption spectrum is different from the fluorescence excited by light corresponding to the peak of band *A*.

### 3. PHOSPHORESCENCE

As in the single crystal phosphors, fluorescence is excited by light absorbed in band *A* alone; for instance a KCl-Tl phosphor shows no phosphorescence under the action of the light from an iron spark transmitted through a Jena filter UG5 which is opaque to light of wave-length shorter than 2400A. However, the full radiation from an iron spark, or in the case of the chloride phosphors even better of an aluminum spark, is able to excite the visible and the ultraviolet emission bands to a long-lasting phosphorescence. As Pohl's collaborators have shown, this phosphorescence is due to light absorption in a second absorption band *C+B*, with a peak at 1950A for the chloride and at 2000A for the bromide phosphor.<sup>3</sup> While our phosphors are thus quite similar to the single crystal halide phosphor as far as the excitation spectrum is concerned, they differ widely with regard to the duration of the afterglow and the shape of the decay curve. In the single crystals the phosphorescence is rather short lived, the decay being completely or nearly exponential with a half-life not exceeding one minute,<sup>6</sup> and the ultraviolet emission band seems also to prevail in the phosphorescence spectrum, as already pointed out. With the new phosphors of high Tl concentration the visible luminescence could be perceived easily in a dark room several hours after the end of the excitation. The decay curve of the visible bands was recorded photographically by means of a photoelectric cell and a string galvanometer during the first two minutes and later by visual readings. Much more elab-

<sup>6</sup> W. Buenger and W. Flexig, *Physik. Zeits.* **67**, 42 and **69**, 637 (1931).

orate measurements were made over much longer periods for the ultraviolet band of a chloride phosphor, using a Geiger-Mueller counter. A comparison between the results of both series of observations showed complete agreement, so that it is sufficient to treat the counter measurements alone, which were in general extended over several hours and in some cases over 24 hours and even two days.

Readings of the telephone counter, which was operated by the Geiger-Mueller tube through an amplifier system and a scaling circuit, were taken every ten seconds during the first three minutes, then every thirty seconds, and later with ever-increasing intervals. The method, which proved to be very satisfactory, does not directly provide the instantaneous intensity  $I$  of the luminescence nor Lenard's "light sum  $L$ ," but the total light energy  $S$  emitted, since the end of the excitation  $S$  is complementary to  $L$ :  $S = L_0 - L$ ;  $I$  is obtained by differentiation of  $S$  or  $L$ . If  $n_0$  is the number of light quanta stored in the phosphor at the end of the excitation, or the number of excited "centers" at the time  $t_0$ , the following relations hold:  $S(t) = \int_0^t I dt = n_0 - L(t)$ . From these relations one derives for the case of an exponential decay or a monomolecular process:

$$I = bn = bn_0e^{-bt} = I_0e^{-bt}; L = n_0e^{-bt}; S = n_0(1 - e^{-bt});$$

and for the case of a parabolic decay or a bimolecular reaction:

$$I = \frac{an_0^2}{(an_0t + 1)^2} = \frac{I_0}{[(aI_0)^{\frac{1}{2}}t + 1]^2};$$

$$L = \frac{I_0^{\frac{1}{2}}t}{aI_0^{\frac{1}{2}}t + a^{\frac{1}{2}}}; S = \frac{I_0t}{(aI_0)^{\frac{1}{2}}t + 1}.$$

The following are the main results of these measurements.

(a) During the first ten minutes after the end of the excitation the decay of luminescence can be represented with deviations of less than one percent by a parabola. From  $t=15$  minutes to  $t=60$  minutes the decay was represented with equally good agreement by an exponential curve with a mean lifetime of a little over 50 minutes. The intervening time from  $t=10$  to 15 minutes could be very well approximated by the superposition of the two curves. For

the longer period of 24 hours a somewhat longer mean life ( $1/b$ ) of about 70 minutes had to be introduced into the exponential.

(b) The color of the visible afterglow was also shifted from blue towards a greenish white with increasing Tl content of the phosphor. An influence of the wave-length of the exciting light (Al or Fe spark) upon the color of the phosphorescence could not be observed. In the phosphors of smaller Tl concentration the visible phosphorescence as a whole was relatively weak, while the ultraviolet phosphorescence was still quite as strong as in the phosphors with greatest Tl content. The decay curves of the ultraviolet phosphorescence had the same general trend for all these phosphors.

(c) It was not possible with the highest available primary light intensities to obtain "full" or saturated excitation of the phosphors. An increase of the duration of excitation, which was varied between 10 sec. and 2 min., also enhanced the initial intensity and the total light output, but in this case the increase tended toward a maximum, if the intensity of the exciting light was always the same.

(d) The phosphorescence intensity was strongly stimulated at any point of the decay period by a rise of temperature, even by a few degrees. If, at room temperature 24 hours after the end of the excitation, the counter gave only a very slow response and no visible radiation could be perceived any more, the counter would again become quite lively and the visible emission would flare up as soon as the phosphor was heated to 50°C. By heating the phosphor immediately after the end of the excitation to 80°C the total energy stored in the phosphor was emitted within a few minutes. However, in contradistinction to Lenard's phosphors and also to the KCl-Tl phosphor of Buenger and Flexig the light sum  $L$  did not remain constant under these conditions. Heating produced, apart from "stimulating," a strong quenching effect; the total light sum fell at 80° to about 25 percent of what it would have been at room temperature.

(e) The light emission of the excited phosphor could be stimulated by irradiation with light of wave-lengths greater than that able to excite the phosphor. All mercury lines, from the near ultraviolet (3600Å) to the yellow part of the

spectrum, as well as red light from an incandescent lamp with a red color filter, produced the effect, which had a certain inertia. When the stimulating irradiation was screened off, the phosphorescence intensity remained above the level to which it had fallen before the stimulation for more than one minute. After very intense irradiation with stimulating light the initial enhancement of the luminescence was followed by a marked decrease of luminosity. Stimulation by light irradiation produces extinction (loss of total light sum) to a much smaller degree than stimulation by heating, if at all. If an excited phosphor instead of being kept in the dark is exposed for some time to daylight or an electric light, the phosphorescence observed afterwards is much weaker than it would have been without this interruption.

#### 4. DISCUSSION

The absorption spectra of the single crystal KCl-Tl phosphors have been ascribed by Seitz<sup>7</sup> to the transition between the  $6S_0$  and the four  $6P$  states of the  $Tl^+$  ion which are supposed to be displaced by the Madelung potential in such a way that the wave-lengths characteristic of the isolated  $Tl^+$  ion (at 1321 and 1908Å) appear in the spectrum of the crystal as bands with peaks at 1950 and 2475Å. Seitz' calculation shows that a shift of this order can be obtained by plausible numerical assumptions. These assumptions, however, are not free of arbitrary elements and there are several facts which do not fit into the picture. It seems strange that the complex thallos halide ions formed in the aqueous solution should have the same absorption bands as the crystal phosphors, if in the latter the impurity metal should occupy the regular place of a  $K^+$  ion in the lattice. At lower halide concentrations of the aqueous solutions the absorption band A of Seitz' terminology becomes less sharp and is displaced toward shorter wave-lengths until it is merged in the shorter wave-length absorption band ( $B+C$ ) which is still strong at KCl concentrations = 1 molar.

O. Hahn takes it for granted that radioactive lead is not incorporated in KCl crystals in the

form of simple ions replacing  $K^+$ , but that it forms some kind of complex negative  $Pb+Cl$  ions which are fixed at defective spots of the lattice. The same might be true for the KCl-Tl phosphors and the identity of the absorption spectra of the phosphors and of the liquid solutions would be explained by the fact that they both originate from the same complex. The shift of band A in solutions of smaller concentration would be due to the formation of complex ions containing a smaller number of halide ions.

Thus it should at least be taken into consideration whether the new absorption bands of the complex metal-halide ions, in the case of thallium as well as in that of  $Cu^+$  or  $Pb^{++}$  and others, are not due to transitions of an electron from a halide ion to the metal cation, rather than to the transition from the ground level to some excited state of the metal ion. It must be kept in mind that the electron affinity spectra of the halide ions in aqueous solution have also their first absorption band not far below 2000Å, and that these bands might well be shifted to greater wave-lengths by the action of a nearby positive metal ion.

Whatever the correct explanation for the origin of the absorption bands may be, the large difference between the wave-length of the absorption and the emission bands must be understood in this case, as in the case of many other phosphors, on the basis of the Franck-Condon principle. The nuclear configuration of the excited "center" after restoration of thermal equilibrium differs widely from the configuration in the normal state, and while the latter is preserved during the absorption process, the former is still present at the end of the emission process, as pointed out in the second edition of *Handbuch der Physik*.<sup>8</sup> Even so it is not easy to see how strong fluorescence bands reaching into the red part of the spectrum could be explained by Seitz' energy level scheme. It would be hardly worth while to propose any potential curves by which the strange dependence of the relative intensities of the fluorescence bands on the wave-length of the exciting light could be represented.

<sup>7</sup> F. Seitz, J. Chem. Phys. **6**, 150 (1938).

<sup>8</sup> *Handbuch der Physik* (1933) Vol. 231, p. 284. Seitz gives the same explanation, quoting a paper by Hippel, Zeits. f. Physik **101**, 680 (1936).

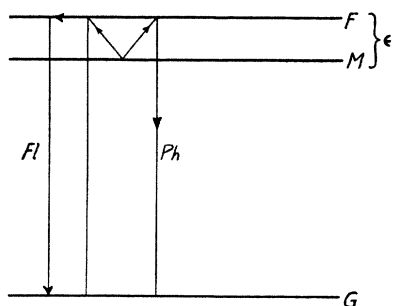


FIG. 3. Energy levels for excitation of phosphorescence.

One of the main arguments in favor of Seitz' theoretical deductions was the fact that no photo-conductivity was excited in the crystals simultaneously with phosphorescence. This indicated that the excited electron is not raised into a free conduction level but is retained within the sphere of attraction of the  $Tl^+$  ion and thus the whole process is a monomolecular one. The experiment proving the absence of photo-conductivity is not quite convincing since it was performed only once with a crystal of not very high  $Tl^+$  concentration and therefore showing only weak phosphorescence. On the other hand the pure parabolic shape of the initial branch of our decay curves cannot be taken as a proof for a bimolecular reaction. The dependence of the initial slope of the decay curve on the initial intensity is a much more decisive criterion than the shape of the curve. For a bimolecular reaction the slope should become much steeper with increasing values of  $I_0$ , while in our case the slope remained unchanged when  $I_0$  was increased in the ratio 1/10. This is the typical behavior of a monomolecular reaction. The deviation from a simple exponential curve would then have to be explained by the superposition of several exponentials.<sup>9</sup>

The persistency of phosphorescence stimulation by long wave-length radiation is perhaps able to throw more light on the problem. The

<sup>9</sup> The same is apparently true for the decay of the long lasting phosphorescence of sulfide phosphors observed by Lenard. Lewshin tried to represent it by parabolic curves and thus to explain the phenomenon as a "recombination luminescence." Lenard's own representation of his observations by superimposed exponential curves is beyond doubt the correct one. Probably all long lasting phosphorescence processes belong to the monomolecular class, because they are exclusively dependent on the probability of the trapped electron's escaping the trap.

same phenomenon is observed with many sulfide phosphors. The simplest energy level scheme representing phosphorescence is the one of Fig. 3 where  $M$  is metastable or rather "quasistable"\* and a "center" raised by light absorption into the state  $F$ , which might or might not be a free conduction band, can either return to the ground state  $G$  with emission of fluorescence or can be "trapped" in the somewhat lower state  $M$ . If the energy difference  $F-M=\epsilon$  is not too large the centers return to  $F$  by the fluctuations of the thermal energy and the emission of the same radiation follows as phosphorescence. The return from  $M$  to  $F$  could be "stimulated" by absorption of long wave radiation with  $h\nu=\epsilon$ , but this effect would have no persistency. In order to explain the inertia of the stimulation it has been suggested by R. P. Johnson<sup>10</sup> that the state  $M$  is not a single narrow level but rather a series of such levels forming a broad band with its upper limit quite close below the state  $F$ . When, by the phosphorescence process, the higher parts of  $M$  have been depopulated, an energy redistribution should be produced within  $M$  by stimulating infra-red radiation. It is easy to see how this would also explain the deviations of the decay curve from a simple exponential law.

However, this scheme is much too primitive to represent the behavior of our phosphors and probably of any other mineral impurity phosphor. If the individual levels of  $M$  can intercombine under the action of infra-red radiation, thermal equilibrium must be reached for the distribution within  $M$  in a time interval exceedingly short as compared to the time intervals observed in phosphorescence processes. Thus the transition probability from  $M$  to  $F$  would be constant at a given temperature exactly as if  $M$  were a single quasistable level.

While  $\epsilon$  cannot be more than of the order of 0.1 eV (or there would be no phosphorescence at room temperature), the stimulating light is in our case by no means long wave infra-red but corresponds to energies of several electron volts.<sup>11</sup> And since  $M$  can be located not more than 0.1

\* I propose the term "quasistable" for long-lived excited states which owe their stability not to the electronic selection rules but to the Franck-Condon principle.

<sup>10</sup> R. P. Johnson, J. Opt. Soc. Am. 29, 387 (1939).

<sup>11</sup> The same is true for the stimulation of most sulfide phosphors.

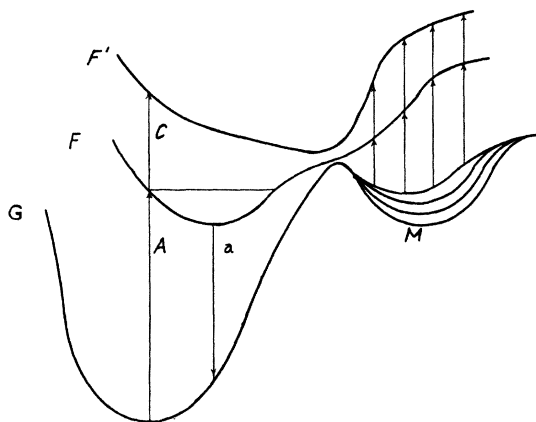


FIG. 4. Potential curves for a phosphor with non-exponential decay.

electron volt below  $F$ , the absorption of stimulating light raises the centers to levels far above  $F$ .

Still another argument against the scheme of Fig. 3 is the following. It is very improbable that  $M$  is located below  $F$  because absorption of light in the band  $A$ , though exciting fluorescence, does not excite phosphorescence. There is of course no reason why  $M$  should not be placed higher than  $F$ , as long as there is a potential barrier of sufficient height separating  $M$  from  $F$ . Mott<sup>12</sup> seems to have been the first to propose potential curves representing such states for the explanation of phosphorescence phenomena, as in Fig. 4. Absorption in band  $A$  would not be able to transfer an electron into the trough at  $M$ , while absorption in band  $C$ , raising the center into the state represented by curve  $F'$ , could bring a part of the electrons into the quasistable state  $M$ . The other part would go over into state  $F$ , from where the emission takes place. The scheme thus constructed is similar to the one proposed by Seitz, without involving his rather specialized assumptions. As the only additional feature, the troughs representing  $M$  have not the same depth for different centers. This is not an improbable assumption in crystals with a lattice strongly perturbed by high concentration of impurities. In the process of phosphorescence the more shallow troughs are the first to be depopulated and thereby the deviation of the decay curve from a simple exponential

<sup>12</sup> N. F. Mott, Proc. Phys. Soc. **49**, 37 (1937).

is explained.<sup>13</sup> Stimulation by light absorption raises electrons from the different  $M$  troughs into potential curves  $F$  or  $F'$  or some other higher level and then light emission or return to  $M$  takes place. However, a partial repopulation of the shallow  $M$  troughs, previously depopulated by the phosphorescence process, can only occur, if by the absorption of "stimulating" light electrons are raised into a free conductivity band. The non-existence of photoelectric conductivity as a consequence of light absorption in excited centers has at least never been proved for KCl-Tl phosphors. It would be analogous to the photoconductivity produced in colored rocksalt by light absorption in the so-called  $F$  centers.<sup>14</sup> By a redistribution of electrons among the different  $M$  troughs the persistency of the stimulation effect would be explained. If this hypothesis should be disproved experimentally, the only alternative hypothesis seems the assumption of a second metastable level intervening between the absorption of stimulating radiation and the final "stimulated" emission process. On the other hand, the stimulation by heating increases the probability of a direct passage from  $M$  to  $G$  and produces thereby a loss of light sum.

In all crystal phosphors the existence of lattice defects seems essential for the formation of "electron traps." Seitz has discussed in detail the reason for the steep increase of phosphorescence intensity with increasing thallium concentration in KCl-Tl phosphors, assuming a quadratic relation between the two. Without introducing any specified hypothesis concerning the interaction of two neighboring thallium ions, it is certain that with increasing amounts of impurities the crystal lattice as a whole will be more distorted and that the defective spots in the lattice which are characterized by potential curves with  $M$  troughs (as in Fig. 4) will become more numerous. The phosphorescence yield, that is the ratio between *absorbed* energy and phosphorescence intensity, should increase in the same proportion.

<sup>13</sup> In the single crystal phosphors of Buenger and Flexig with a relatively low Tl concentration the decay curve is completely or very nearly exponential from the first start of the phosphorescence process.

<sup>14</sup> Reimann [Nature **140**, 501 (1937)] has shown that the "stimulation" of excited sulfide phosphors is accompanied by photoelectric conductivity.

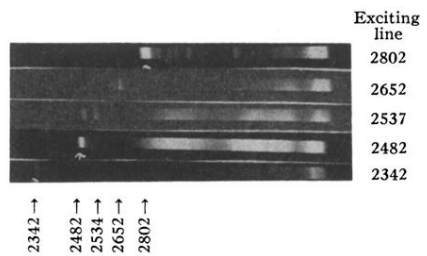


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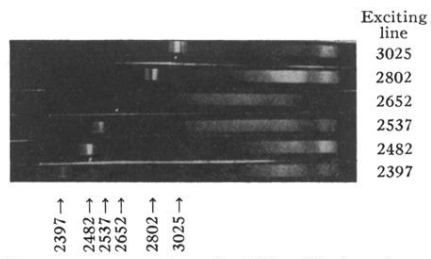


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