

the z axis (and the product of these with the inversion). Hence, the point group has only the very low symmetry of C_{2h} (or $2/m$). If the particular crystal did not support an internal strain belonging to Γ_8 , however, the additional symmetry elements of twofold rotation around $[110]$ and $[\bar{1}\bar{1}0]$ would survive, and the point group would be D_{2h} [or $(2/m)(2/m)(2/m)$]. Thus, examination of the crystal symmetry, by x-ray dif-

fraction, as a function of the direction of (sublattice) magnetization can give interesting information as to the magnetoelastic coupling.

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Infrared Light Stimulation and Quenching in ZnS Phosphors*

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The effects of infrared on the luminescence of three ZnS phosphors (activated with Cu, Ag, and Cu-Pb) at liquid nitrogen temperatures has been investigated. The transient stimulation and permanent quenching (or enhancement) was determined at various wavelengths in the emission spectrum of the ultraviolet-excited phosphors. Two infrared bands were used, one at about 0.75, the other at about 1.3. The effect of the infrared varies with the emission wavelength but not sufficiently to explain discrepancies with the usually accepted phosphor model. A modification of this model consisting of a coupled trapped electron-ionized activator complex is proposed, and the consequences are discussed.

I. INTRODUCTION

In a previous paper (hereafter called I), Kallmann and Luchner¹ have reported on measurements concerning the mechanism of ir (infrared) light stimulation in ZnS-type phosphors. The main result was that such stimulation cannot be brought about by an independent direct release of trapped electrons as was often assumed. It was shown that many effects concerning stimulation could be understood with the assumption that the ir somehow produces a faster recombination between conduction electrons and ionized activators, which leads to a transient increase in luminescent intensity. In order to provide a model for stimulation and quenching, it is necessary to find out more about the mechanism by which the ir produces faster recombinations and quenching at the same time, as indicated by many experiments. The present paper deals with this question and proposes a model for trapping of electrons and this release by ir which is somewhat different than envisaged up to now.

Before the experiments and their interpretation are given, we will summarize numerous discrepancies be-

tween the "old" model which has been rather successfully used up to now,² and results already obtained.

(1) Both stimulation and quenching of luminescence and photoconductivity by infrared evidence the same infrared wavelength dependence³⁻⁶ showing that they are produced by the same elementary process. This cannot be understood by using the assumption that stimulation is due to the independent release of electrons from traps and that quenching is due to the independent release of holes from ionized activators.

(2) The equilibrium quenching of luminescence (due to infrared) is less than that of the photoconductivity⁷; if the light emission is proportional to the product of n and P_t (see paragraph 4 below), light quenching should be greater.

(3) Infrared stimulation of luminescence after excitation is not instantaneous but has a finite rise⁸; this

² M. Schön, *Z. Physik* **119**, 463 (1942); H. A. Klasens, *Nature* **158**, 306 (1946).

³ I. Broser and R. Broser Warminsky, *Z. Elektrochem.* **61**, 209 (1957).

⁴ F. G. Ullmann and J. J. Dropkin, *J. Electrochem. Soc.* **108**, 156 (1961).

⁵ H. Kallmann, B. Kramer, and A. Perlmutter, *Phys. Rev.* **99**, 391 (1955).

⁶ P. Wachter (to be published).

⁷ B. Kramer and H. Kallmann, *International Conference on the Luminescence of Organic and Inorganic Materials*, edited by H. P. Kallmann and G. M. Spruch (John Wiley & Sons, Inc., New York, 1962).

⁸ M. Sidran, Ph.D. thesis, New York University, 1955 (unpublished), and H. Kallmann and E. Sucov, *Phys. Rev.* **109**, 1473 (1958).

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¹ H. Kallmann and K. Luchner, *Phys. Rev.* **123**, 2013 (1961).

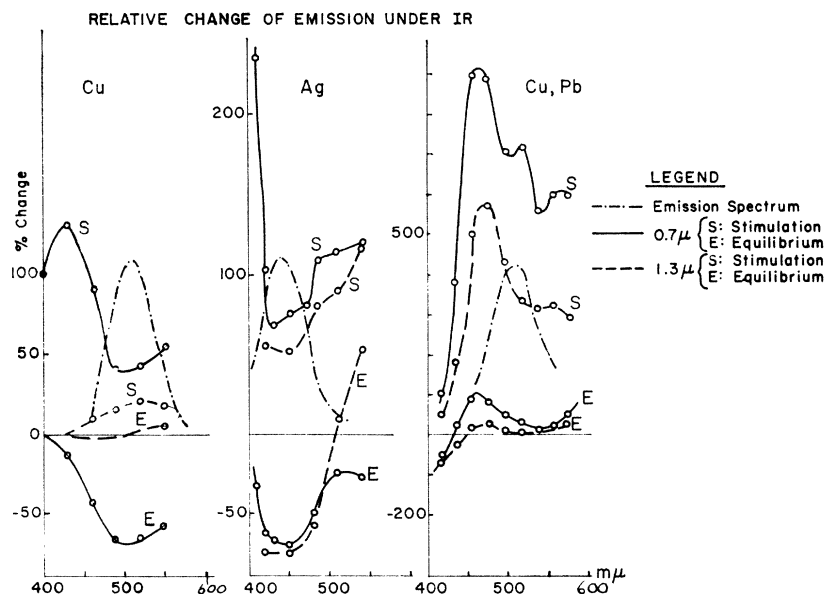


FIG. 1. Stimulation peak ($S = \Delta I' / I$) and equilibrium value ($E = \Delta I'' / I$) obtained when infrared is added to phosphor excited by 3660 Å irradiation. Negative values of E indicated quenching.

buildup is longer for longer decay periods. This cannot be ascribed only to the filling of empty shallow traps by electrons released from deeper traps because a freshly excited sample, whose shallow traps are not filled to saturation, shows a fast rise.

When many deep traps are filled (as shown by consequent glow curves) but when the conductivity is low (exhaustion of shallow traps), the addition of infrared produces negligible instantaneous luminescent stimulation. Increasing the photoconductivity, by heating for instance, restores infrared-induced light stimulation.⁶ The emptying of shallow traps by partial heating, and recooling decreases instantaneous light stimulation considerably; reheating restores it but the rise of stimulation upon turning on the ir is still gradual.

(4) The luminescence at constant excitation does not change very much upon cooling from room to low (liquid nitrogen) temperatures, while the photoconductivity remains about the same or even increases.⁶ This does not agree with the well-known expression $\alpha I / \beta^* P_i = n$ (αI = excitation, n = density of free electrons, P_i = density of ionized activators, β^* temperature independent) since P_i increases by a factor of about 100 over this range. A change in mobility cannot be responsible for this fact, since the mobility does not change by such a factor upon cooling.

(5) The investigation of a paramagnetic resonance signal in excited phosphors⁹ has shown that most phosphors do not show a signal even if the traps are saturated at low temperature. Even in these special phosphors which show electron paramagnetic resonance the number of electrons responsible for the signal is much less than the number trapped.

(6) Immediately after excitation, the decay of light is very much faster than that of conductivity⁶ even though the number P_i changes very little in this interval.

Many of these discrepancies can be overcome by assuming that activators of different effective β^* exist, and that the action of infrared (and of temperature change) is to shift holes from some types of activators to others.^{1,10} One would expect, therefore, that infrared (and temperature change) would change the emission spectrum considerably.

It is known that there is some shift in emission spectra with temperature, but for many phosphors showing the above discrepancies this shift is very slight; thus there is no evidence of a strong change with β^* due to temperature.

To test the action of infrared on the emission spectrum, the quenching and stimulation at various emitted wavelengths has been studied.

II. EXPERIMENTAL PROCEDURE

The experimental arrangement was similar to that in paper I. A silver, a copper, and a copper-lead activated ZnS sample were excited by 3650 Å light at liquid-nitrogen temperature and the spectral distribution of the emission was measured with and without ir irradiation. An ir band around 0.7 μ and one around 1.3 μ were used. When ir is turned on, a transient light stimulation ($\Delta I'$) and a permanent quenching ($\Delta I''$) are observed. Their relative values $\Delta I' / I$ and $\Delta I'' / I$ are given as S and E , respectively, for the two ir wavelength bands where I is the equilibrium light emission without ir. Their relative rather than their absolute values are given in order to show the amount of spectral shift more clearly.

⁹ H. Kallmann, J. Gallagher, and N. Worthespoon, *Fifth International Symposium on Free Radicals, Stockholm, Sweden, 1961* (Gordon and Breach Publishers, New York, 1961).

¹⁰ B. Kramer, M. Schön, *Z. Physik* **160**, 145 (1960).

If all activators would have the same β^* and the shape of the emission band was due only to an interaction with the lattice, for instance, one would expect the $(\Delta I/I)$'s to be the same for all wavelengths emitted although the ΔI 's would vary strongly according to the intensity of the band.

III. RESULTS

The results are best summarized by Fig. 1 in which $\Delta I'/I$ and $\Delta I''/I$ are given as functions of the emitted wavelengths. A different relative quenching and stimulation across the emission band is clearly seen for Cu-, as well as for Ag-, and (Cu, Pb)-activated samples. The quenching is strongest in the middle of the band and weakest at the edges. Only for the Cu-activated phosphor under 1.3μ is the permanent quenching weak. We know from other experiments that there is also some quenching in this region depending upon the coactivator concentration.

On the other hand, the relative stimulation is strongest at the edges of the band, except for the 1.3μ copper case. It may be further noted that for the copper case the emission from wavelengths shorter than 4510 \AA is almost zero; this means that in this phosphor the blue copper band was negligibly small. The silver phosphor has a small band at 3800 \AA , as seen with x-ray excitation,⁶ but the intensity ratio between this band and the main band is not appreciably changed by infrared.

It must be kept in mind that the values given in Fig. 1 are relative values. The I 's themselves are by far largest in the middle of the band, except perhaps for the Ag case under 0.7μ irradiation. A similar situation prevails for quenching; the total amount of light decrease is by far largest in the middle of the band. The Cu 1.3μ experiment shows a strong transient stimulation in the middle of the band.

In the (Cu,Pb)-activated phosphor, the over-all effect of ir in the equilibrium is that of enhancement. This indicates that without ir some radiationless transitions occur which are overcome by ir. The transient relative stimulation is very strong at the short-wavelength side of the band, so that a definite blue shift is observed under 0.7μ ir irradiation, which even prevails in the equilibrium.

The results that the relative quenching and stimulation are different for various parts of the emission spectra show that these emission bands cannot be interpreted as originating in one activator level in interaction with the lattice. Rather, these emission bands must be due to at least three different levels, each with a different response to infrared.

IV. INTERPRETATION OF RESULTS

The above results show that although some shift of the emission spectra does occur when infrared radiation is applied, these shifts are too small to explain the effects described above (Sec. I).

If a shift of holes by ir from activation levels with small β^* to those with larger β^* would account for light stimulation, one would expect that some portions of the emission spectrum would be quenched while others are stimulated at the same time. Figure 1, however, shows that stimulation exists over the entire spectrum, the "wings" showing greater relative stimulation than the center of the band. But the absolute enhancement is by far largest in the middle of the band. In order to explain this by the assumption of activators with different β^* , one would have to stipulate that many activators—indeed, a majority of them—exist, which have a negligible β^* so that the emission from these activators is not noticeable. This is certainly a very unlikely assumption.

Therefore, apparently the postulation of activator levels with strongly different β^* 's alone is not sufficient to explain these experiments; one has to find a different mechanism which, above all, explains the close relationship of stimulation and quenching on ir wavelength, and include the assumption of different β^* 's in some way. In order to satisfy this condition, the following model is proposed.

(1) Trapped electrons exist mainly in the neighborhood of ionized activators and are coupled to them.¹¹

(2) An infrared quantum is absorbed by the ionized activator-trapped electron complex. This energy can be dissipated in the various ways listed below similar to the excess energy given off in molecules due to the Franck-Condon effect.

(a) It may be transferred to the crystal by lattice vibrations with the complex returning to its original state.

(b) Part of this energy may be used to raise the trapped electron to an intermediate level (below the conduction band) from which it can radiatively recombine with the ionized activator without passing through the conduction band. This produces light stimulation.

(c) The energy is partially used to release an electron to the conductivity band. This produces conductivity stimulation.

(d) The energy is used to free electrons and holes. This process may lead to radiationless transitions (quenching), or the electron and hole may be shifted to another activator. This process (d) occurs only with a small probability under long-wavelength infrared ($\sim 1.3\mu$) for some phosphors at low temperature. Apparently this process requires some additional thermal energy.

These assumptions describe a coupled system consisting of the trapped electron, an excited level, and the ionized activator. Using this model, some of the difficulties detailed above can be resolved.

¹¹ The association of an activator-coactivator pair in ZnS-type phosphors has been postulated theoretically by J. S. Prener and F. E. Williams, *Phys. Rev.* **101**, 1427 (1956); this would lead to a coupled trapped electron-ionized activator system if the coactivators act as trapping centers.

The essential feature of this model is that the electrons are not only trapped in the neighborhood of ionized activators, but are actually coupled to them. The ir light is absorbed by the ionized activator, but because of the above-described coupling the trapped electrons can be affected.

Differences in the degree of this coupling could give rise to different activator levels with varying response to infrared as discussed in the last paragraph of the previous section.

Since the absorption of an infrared quantum is followed by either (a), (b), (c), or (d), such an absorption can result either in a release of a trapped electron or a simultaneous release of a trapped electron and a hole or in a direct stimulation. In this way the similar dependence of stimulation and quenching on infrared wavelength comes about (discrepancy No. 1).

Process (b) described above brings a radiative recombination about without a corresponding increase in free electrons and thus in conductivity. Thus, ir temporarily may increase the number of light-emitting processes. That light quenching is less than the conductivity quenching is due to the fact that both processes (b) and (d) reduce the free-electron concentration, but only the nonradiative one reduces the light-emitting process (discrepancy No. 2).

Apparently the relative probabilities of processes (a), (b), (c), and (d) also depend upon the energy level in which the electrons are trapped. There are different levels as evidenced by glow curves. It seems that the shallow trap levels have a higher probability for the stimulation process (b). This would explain the observation that when the shallow traps are emptied at low temperature, the stimulation effect is much weaker (discrepancy No. 3).

Because of the excited level in this coupled system, a light-emitting process can occur which is not proportional to the concentration of free electrons in the conductivity band; thus the equation $n = \alpha I / \beta^* P_i$ does not always hold (discrepancy No. 4).

The coupled system (trapped electron and ionized activator) gives a net magnetic moment of zero. Only isolated trapped electrons or trapped holes can give a paramagnetic signal and such a condition occurs only in a few, special phosphors (discrepancy No. 5), although other reasons may also be responsible for the absence of such signals.

The relative fast drop in light emission is mainly due to the transition involving the excited state of the coupled system and does not directly involve the free-electron concentration. Thus, the conductivity may decay at a slower rate (discrepancy No. 6).

A special remark is required to explain the equilibrium behavior of the ZnS:Cu,Pb phosphor which shows an appreciable net enhancement when short-wavelength infrared is added to the uv excitation. This indicates that a quenching process which occurs under uv excitation alone is decreased when infrared is added. The infrared may shift the holes from Cu to Pb centers; if the latter has a faster transition probability the quenching process is reduced.

V. SUMMARY

The identical wavelength dependence of ir quenching and stimulation, the lack of correlation between luminescence and conductivity expected according to the Schön-Klasen model, the slow rise of ir-stimulated light upon ir irradiation and the observed but relatively small wavelength shift of the fluorescent light upon ir irradiation are interpreted to mean that ionized activators and trapped electrons form a complex. The absorbed ir energy can be dissipated in various ways: either to produce electrons and holes (quenching) or only free electrons (current stimulation) or to raise electrons to an intermediate level, which leads to light stimulation.

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