Effect of Infra-Red on Emission and Trapping in ZnS:Cu Phosphors*†

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September 22, 1950

A STIMULATION band for ZnS:Cu phosphors has been found by Garlick and Mason,[1] and by the author, at about 1.2 to 1.3 microns. Daly[2] reported a stimulation band at 1.26 microns for a (Zn:Cd)S:Cu phosphor, as well as bands at 2.08 and 2.70 microns. Garlick and Mason attributed the band at 1.3 microns to the copper.

This letter reports the results obtained when a series[3] of hex.—ZnS:Cu(0.0–0.3), [NaCl(2)] phosphors[4] are stimulated by a broad band of infra-red, ranging in wave-length from approximately 0.8 to 3.0 microns. It is found that (1) there is a marked spectral shift to the blue in the stimulated emission, (2) the intensity of the stimulated emission does not depend simply on the number of electrons freed from traps by the infra-red, and (3) the extent of trap emptying by infra-red is a function of the temperature of stimulation.

The hex.—ZnS:Cu(0.0–0.03), [NaCl(2)] phosphor series has both blue and green emission bands. The variation of the spectral emission with copper proportions has been discussed elsewhere.[4] Pertinent for the discussion here is the fact that the blue band decreases in intensity, whereas the green band increases in intensity, for copper proportions between 0.0001 and 0.03 percent.

At room temperature, it was found that both the flash-up on application of the infra-red to a decaying phosphor (after an initial excitation by 3650A ultraviolet), and the phosphorescence emission during infra-red illumination were bluer than the unstimulated emission, for phosphors with 0.0001 to 0.003 percent Cu. A Wratten 47 filter was used to isolate the blue emission, and a Wratten 62 filter to isolate the green emission. Figure 1a shows the initial flash-up under infra-red for nine phosphors with increasing copper proportion, the infra-red being applied after one minute of decay. A complete decay cycle, before and during infra-red, is shown in Fig. 1b, for hex.—ZnS:Cu(0.001), [NaCl(2)].

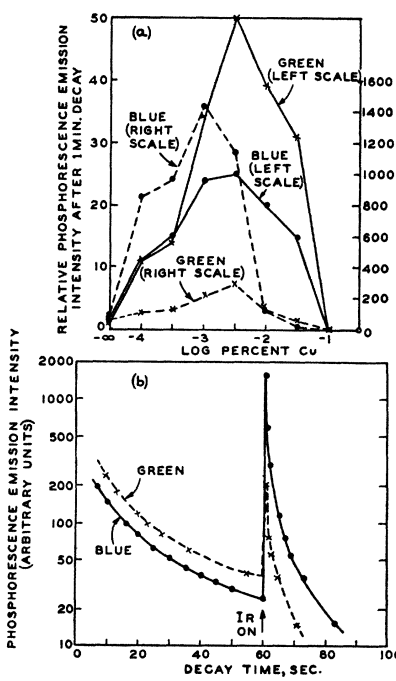

FIG. 1. (a) Phosphorescence emission intensity at room temperature after one minute decay, and flash-up intensity under infra-red stimulation as a function of copper proportion in hex.—ZnS:Cu(0.0–0.3), [NaCl(2)] phosphors. (b) Phosphorescence emission decay at room temperature before and during infra-red illumination for hex.—ZnS:Cu(0.001), [NaCl(2)].

TABLE I. Release of electrons from traps by infra-red.

Percent Cu	Relative no. of electrons freed by *IR* at −196°C in 18 min.	Relative no. of electrons freed by *IR* at 22°C in 4 min.
0.003	100	35
0.01	115	37
0.03	75	13
0.1	70	No traps present
0.3	40	No traps present

For no copper, the stimulation of blue and green emission as obtained from the filters is about the same, since the spectral emission consists only of a blue band with a long tail into the green. For 0.01 percent copper and above, little stimulation of any type occurs.

A study of the infra-red emptying of traps was made as a function of temperature using glow curve techniques. The phosphor is excited at temperature T, and is then allowed to decay at T for t minutes before a glow curve is run. The phosphor is then recooled to T, re-excited, and allowed to decay for t minutes with the infra-red on before a second glow curve is run. The difference between the area under the glow curve obtained after the t minutes of decay and infra-red, and the area obtained after t minutes of decay without infra-red, gives at least the minimum number of electrons freed from traps by the infra-red. Table I gives the results of such measurements. These results show that the decrease in the stimulation flash-up between 0.003 and 0.01 percent Cu is not caused by a decrease in the ability of the infra-red to empty traps.

The temperature dependence of the emptying of traps by infra-red is demonstrated by the glow curves of Fig. 2. Deep traps, rapidly emptied by infra-red at room temperature, are not emptied at all by infra-red at −196°C for comparable times of stimulation.

The energy corresponding to 1.3 microns is 0.95 ev, which is exactly the energy reported by Garlick and Gibson[5] for the difference between the conduction band and the excited state of the green-emitting center. The absorption of the 1.3-micron infra-red by the green-emitting center would decrease the probability of a transition giving green emission. This would result in a spectral

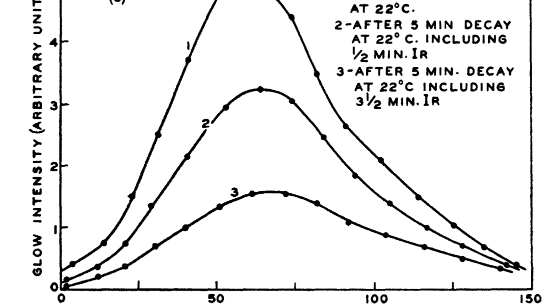

FIG. 2. Glow curves obtained at a heating rate of 0.33 degree Centigrade per second for hex.—ZnS:Cu(0.003), [NaCl(2)] showing the emptying of traps by infra-red, at −196° and at 22°C.

shift to the blue under infra-red stimulation. The large decrease in stimulation between 0.003 and 0.01 percent Cu may be attributed to the large decrease in the number of effective blue-emitting centers (caused by an increase in the relative number of green-emitting centers and hence an increase in the rate of the process by which holes are transferred from blue-emitting to green-emitting centers) as shown by spectral curves.[4]

* This letter is part of a dissertation presented to the faculty of the Physics Department of Princeton University in May, 1950, as partial fulfillment for the requirements of the Ph.D. degree.
† This work was done under contract between ONR and RCA.
[1] G. F. J. Garlick and D. E. Mason, J. Electrochem. Soc. **96**, 90 (1949).
[2] E. F. Daly, Proc. Roy. Soc. **196**, 554 (1949).
[3] Proportions are given in weight percent.
[4] Full discussion of the preparation and luminescence characteristics of these phosphors is included in a paper by the author, R. H. Bube, Phys. Rev. **80**, 657 (1950).
[5] G. F. J. Garlick and A. F. Gibson, J. Opt. Soc. Am. **39**, 935 (1949).

Further Remarks on the Absorption of π^--Mesons in Hydrogen*

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PANOFSKY, Aamodt, and York[1] have measured the γ-ray spectrum arising from the absorption of π^--mesons in hydrogen. As a result, it now appears fairly certain that the two processes hypothesized in an earlier paper,[2] namely: $\pi^-+P\rightarrow N+\gamma$ (radiative absorption) and $\pi^-+P\rightarrow N+\pi^0$ (mesic absorption) actually take place in nature.[3] Apart from the sensitive method which is furnished for the determination of the π^0-mass, the ratio of the mesic to radiative absorption probability determines the strength of the π^0-nucleon coupling. It is interesting to calculate[4] values of the π^0 coupling constant for various possible combinations of π^-- and π^0-fields and couplings.[5] The results are given in Table I. Column 1 contains expressions for the radiative absorption probability from the K-shell, while the remaining columns list expressions for the mesic absorption probability[6] and the values of the π^0-coupling constant (in units of $1/\hbar c$) which follow from the observed equality of radiative and mesic absorption.[7] The quantities g_P and g_N are the π^0-coupling constants with proton and neutron, respectively.

TABLE I. Absorption probabilities per sec.*

Radiative	Mesic		
$S(S)$	$S(S)-S(S)$	$S(S)-PS(PS)$	$S(S)-PS(PV)$
$2e^2\Gamma^2\delta^2$	$4\beta(\Delta g)^2$	$\beta^3\delta^2(\Delta g)^2$	$4\beta^3(\Delta g)^2$
	$(\Delta g)^2=0.008$	$(\Delta g)^2=27$	$(\Delta g)^2=0.15$
$PS(PS)$	$PS(PS)-S(S)$	$PS(PS)-PS(PS)$	$PS(PS)-PS(PV)$
$2e^2\delta^2$	$\frac{\beta^3}{4}\delta^4(\Delta g)^2$	$\beta\delta^2(\bar{g})^2$	$\beta\delta^2(\Delta g)^2$
	$(\Delta g)^2=210$	$(\bar{g})^2=0.06$	$(\Delta g)^2=0.06$
$PS(PV)$	$PS(PV)-S(S)$	$PS(PV)-PS(PS)$	$PS(PV)-PS(PV)$
$8e^2$	$\beta^3\delta^2(\Delta g)^2$	$\beta\delta^2(\Delta g)^2$	$\beta\delta^2(\bar{g})^2$
	$(\Delta g)^2=210$	$(\Delta g)^2=11$	$(\bar{g})^2=11$
$V(V)$	$V(V)-S(S)$	$V(V)-PS(PS)$	$V(V)-PS(PV)$
$(2/3)e^2$	$(4/3)\beta^3\delta^2 g_P^2$	$\beta\delta^2(\Delta g)^2$	$\beta\delta^2(\bar{g})^2$
	$g_P^2=13$	$(\Delta g)^2=0.93$	$(\bar{g})^2=0.93$
$PV(PV)$	$PV(PV)-S(S)$	$PV(PV)-PS(PS)$	$PV(PV)-PS(PV)$
$(2/3)e^2$	$4\beta(\Delta g)^2$	$\frac{\beta^3\delta^2}{3}[(\Delta g)^2+2(\bar{g})^2]$	$\frac{4\beta^3}{3}[(\Delta g)^2+2(\bar{g})^2]$
	$(\Delta g)^2=0.005$	$[(\Delta g)^2+2(\bar{g})^2=52$	$[(\Delta g)^2+2(\bar{g})^2]=0.3$

* The absorption probabilities per sec. are given in units of $\alpha^3\cdot g^2,/\hbar c(\mu c^2/\hbar)\cdot(1/\hbar c)$, $\alpha=e^2/\hbar c$, g is the π^--coupling constant, μ is the π^-- mass $\Gamma=4.71$ =difference between proton and neutron magnetic moments (in units of the nuclear magneton), $\delta=\mu/M$, $\beta=p_0/\mu_0 c$, $\Delta g=g_P-g_N$, $\bar{g}=g_P+g_N$; in the first column, $PS(PV)$ means the absorption of a PS π^- with PV coupling; in column 3, for example, $PS(PV)-PS(PS)$ means the absorption of a PS π^- with PV coupling and the emission of a PS π^0 with PS coupling, etc.

Examination of Table I permits us to discard some of the theories when proper account is taken of other π-meson experiments; e.g., the upper limit of $5\cdot 10^{-14}$ sec. on the lifetime[8] of π^0, the photon production[9] of $\pi^{\pm}$, π^0, etc. Since the very recent experiment on the π^--absorption in deuterium definitely excludes the scalar and vector fields for the charged π-meson,[9a] we shall pursue this analysis here only to the extent of pointing out that Table I provides evidence against a scalar field for π^0: the extremely large π^0-coupling constants predicted by combining a PS field for π^- with a S field for π^0 contradicts the assumption of weak coupling, whereas the extremely small π^0-coupling constants predicted by combining PV for π^- and S for π^0 leads to too long a lifetime for π^0-decay. Thus, the only consistent weak coupling theory which is possible is a PS field for π^0 and a PS or PV field for $\pi^{\pm}$. In order to decide between the PS and PV fields for the charged π-meson, it is necessary to invoke some other experiment; e.g. Brueckner[9] has concluded that the leveling off with energy of the cross section for photon production of π^+ is evidence for the PS field.

Even if we assume that both the charged and neutral π-mesons are pseudoscalar, neither the hydrogen nor the deuterium experiment fixes the nature of the coupling of the PS π-meson to the nucleon. In principle, a linear combination of PS and PV couplings is possible; the ratio, R, of the mesic to radiative absorption probabilities in hydrogen would then become (g_P, g_N, g, now refer to PS coupling while f, f_P, f_N refer to PV coupling):

$$R=\frac{\beta[g(\bar{g}+\Delta f)+f(\Delta g+\bar{f})]^2/\hbar c}{2\alpha(g-2/\delta f)^2}. \quad (1)$$

Equation (1) contains the dominant terms in an expansion in powers of δ; however, if a particular choice of g_P and g_N leads to a cancellation in the mesic absorption probability, the next term in δ has to be considered. For example, in the pure $PS(PS)-PS(PS)$ theory, R vanishes when $g_P=-g_N$; to the next order[10] in δ, $R=(\beta\delta^2/8\alpha)(\Delta g)^2/\hbar c$ so that the choice $g_P=-g_N$ leads to $g_P^2/\hbar c=g_N^2/\hbar c=2\alpha/\beta\delta^2=2.8$ (see Table I). A promising method for deciding between PS and PV coupling is to study the energy dependence of ordinary and charge exchange π-meson scattering by nucleons. PS coupling leads to a decreasing cross section with energy whereas PV coupling yields a rapidly increasing cross section.[11] For the meson energies produced by present accelerators (up to 150 Mev, say) the reaction of the meson field should not seriously modify the qualitative predictions of weak coupling theory.[12]

We are greatly indebted to Professor Panofsky for keeping us closely informed of experimental developments.

* This work is supported by the joint program of the ONR and AEC.
[1] Panofsky, Aamodt, and York, Phys. Rev. **78**, 825 (1950).
[2] R. Marshak and A. Wightman, Phys. Rev. **76**, 114 (1949); see also B. Bruno, Ark. f. Fysik **1**, No. 2 (1949).
[3] A complete demonstration of the latter process would consist, of course, in measuring the two "low" energy γ-rays in coincidence.
[4] We use weak coupling theory; however, strong coupling theory yields similar results for some of the theories, according to a private communication from C. N. Yang.
[5] We have omitted the derivative couplings for the scalar, vector, and pseudovector theories since they do not lead to any essentially new results. Only spin zero theories are considered for π^0 since π^0 decays into two γ-rays.
[6] The $S(S)-S(S)$ expression given in Table I agrees with that given in reference 2 whereas the $PS(PS)-PS(PS)$ expression (Eq. (11)) is δ^2 times smaller. It is *not* true that the equivalence theorem holds for mesic absorption; as a matter of fact, the $PS(PS)-PS(PS)$ and $PS(PV)-PS(PV)$ expressions are *identical*. It is precisely this breakdown of the equivalence theorem for mesic absorption (in contrast to radiative absorption) which makes the hydrogen experiment so interesting and is responsible for some of the surprising numbers listed in Table I.
[7] Panofsky, Aamodt, and Hadley, private communication; $\beta\equiv p_0/\mu_0 c=0.23$ was used where μ_0 and p_0 are the π^0-mass and momentum respectively.
[8] A. Carlson, J. Hooper, and D. King, Phil. Mag. **41**, 701 (1950).
[9] J. Steinberger and A. Bishop, Phys. Rev. **78**, 494 (1950). Steinberger, Panofsky, and Stellar, Phys. Rev. **78**, 802 (1950). K. Brueckner, Phys. Rev. **79**, 641 (1950).