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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1994 Northridge earthquake. The authors estimate that the energy released was approximately 10¹⁵ J. This is a very large amount of energy. The authors also discuss the energy released by the 1964 Chilean earthquake. They estimate that the energy released was approximately 10¹⁶ J. This is even larger than the energy released by the Northridge earthquake. The authors conclude that the energy released by earthquakes is a significant fraction of the total energy released by the Earth. This is a very interesting result. It suggests that earthquakes are a major source of energy for the Earth. The article does not have any references.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

A tunneling model for the decay of luminescence in inorganic phosphors: The case of $\text{Zn}_2\text{SiO}_4\text{:Mn}$

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We have investigated phosphorescence, thermoluminescence, and photostimulated luminescence in manganese activated zinc silicate phosphors, both with and without arsenic doping. Both phosphorescence and photostimulated luminescence intensities are found to decay as the reciprocal of the time, a result which requires a different interpretation from that given by the usual model of electron release from a distribution of trap levels. To account for these results we propose a new model based on the radiative recombination of electrons and holes through tunneling from shallow traps or from excited states of the deeper traps. A simple expression is derived which describes the decay of both types of luminescence in phosphors under very general conditions for which tunneling is the dominant recombination mechanism. Excellent agreement between theory and experiment is found.

I. INTRODUCTION

Luminescent inorganic solids can be classified, according to the decay of their light emission L , into two broad categories¹: those with an exponential decay, $L \propto \exp^{-t/\tau}$, and those with a power law decay $L \propto t^{-m}$. In fact, many materials (especially those assigned to the second category) display both types of behavior—the persistent luminescence, which decays according to a power law, may be preceded by an intrinsic localized luminescence, which decays exponentially. Unlike the exponentially decaying part, whose rate is determined by the lifetimes of the radiative states, the power law decay rate may be sensitive to changes in temperature and to the wavelength and intensity of the excitation. An important and frequently occurring case is the “hyperbolic” case, for which $m=1$, although it should be noted that experiments show deviations from the t^{-1} law at early times.

It is now generally accepted^{1(b)} that the mechanism of t^{-m} phosphorescence involves the release of electrons from various traps in the phosphor and their subsequent radiative recombination with trapped holes. When the rate-determining step is the diffusion of the free electrons to the holes at remote sites the situation can be described by bimolecular kinetics, for which the recombination rate is proportional to the product of electron and hole densities and generates a t^{-2} decay. The origin of the hyperbolic t^{-1} decay is not so straightforward. Randall and Wilkins² provided the first interpretation by considering phosphors with trap levels at many different depths. They showed that when the trap distribution is uniform, phosphorescence decays as t^{-1} . In a later study, Medlin³ discussed the phosphorescence decay of thermoluminescent crystals, such as calcite, dolomite, anhydrite, etc., and pointed out that bimolecular kinetics cannot account for the details of the power law decay

$$L \propto (t_0 + t)^{-m}$$

in such materials, except at temperatures well above the thermoluminescent “glow” peak. He proposed that the discrepancies can be accounted for by first-order decay from a (Gaussian) distribution of trapping levels.

The specific value of m (which can be unity) was determined by the particulars of the trap distribution and by the experimental conditions.

Alternative explanations for the t^{-1} decay are suggested by studies such as that by Delbecq *et al.*,⁴ where a temperature-independent t^{-1} decay law of the luminescence from the recombination of trapped electrons and holes in KCl:AgCl and KCl:TlCl was ascribed to electron tunneling. A simple model, which did not consider the details of the distribution of tunneling centers, was used to show that electron-hole recombination through electron tunneling can, in principle, generate a t^{-1} decay.

In other fields, such as semiconductor luminescence⁵ and recombination luminescence from irradiated organic molecules in organic glasses,^{6,7} analogous observations of approximate t^{-1} decays of recombination luminescence have been made which were interpreted in terms of electron tunneling. It appears that such tunneling models have not previously been applied to the decay of luminescence in phosphors. It is interesting to note that progress in such diverse fields has, apparently, proceeded independently, with little recognition that similar phenomena have been treated elsewhere.

In this article, we develop a model of electron tunneling which can account for the t^{-1} decays in phosphors and related materials. The tunneling is assumed to occur between the radiative recombination centers and either shallow electron traps or the excited states of deeper traps. Special attention is paid to the distribution of occupied traps and recombination centers as a function of the excitation conditions. A general equation is derived which accurately describes the decay of both phosphorescence and photostimulated luminescence, see below, under conditions for which the dominant recombination mechanism depends on electron tunneling. The results of this treatment are compared with experimental results on the decay of luminescence in the phosphors (P1) $\text{Zn}_2\text{SiO}_4\text{:Mn}$ and (P39) $\text{Zn}_2\text{SiO}_4\text{:Mn, As}$.⁸

The manganese-doped zinc silicate material (without arsenic) studied here is a well-known phosphor (P1) useful in cathode-ray tube applications. The manganese

occurs as Mn^{2+} ions located on two nonequivalent zinc sites in the rhombohedral crystal with a tetrahedral site symmetry.⁹ The green luminescence of the material is ascribed to the ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ spin flip transition of the $\text{Mn}^{2+}(3d^5)$ ion¹⁰ and, when excited directly in the Mn^{2+} absorption bands, decays exponentially with a decay time of about 10 ms.¹¹

Excitation with ultraviolet light generates, in addition to this intrinsic emission, a weak but very long-lived luminescence with the same spectral distribution. This long-lived emission (phosphorescence) obviously arises from some type of electron-hole recombination process, as was demonstrated by the early work of Randall and Wilkins.¹² This work showed, through studies of thermoluminescence, that the crystal possesses electron trap states which can be filled by ultraviolet light. A few years later, Garlick and Gibson¹³ observed that the room temperature decay of phosphorescence in this material was not exponential but followed a hyperbolic decay law. These workers explained this result by assuming that the trap levels were distributed over a (continuous) range of energies and that retrapping of released electrons was absent.

In addition to the phosphor P1, we have studied a doubly doped material with arsenic as the second dopant $\text{Zn}_2\text{SiO}_4:\text{Mn}, \text{As}$, known as phosphor P39. It was shown by Froelich and Fonda¹⁴ that the arsenic doping enhances the long-lived phosphorescence, although the reason for this enhancement is not fully understood.

In our study of these two phosphors we first investigate, through thermostimulated luminescence measurements, the properties of the electron trap states. We then follow the emptying of these traps through thermo- or photostimulation and study the decay dynamics of the resulting electron-hole recombination emission. Finally, we compare our decay measurements with the predictions of a general model of tunneling luminescence.

II. EXPERIMENTAL TECHNIQUES

Three types of experiments—phosphorescence, thermostimulated luminescence (TSL), and photostimulated luminescence (PSL)—are described in this paper, and in all cases the green Mn^{2+} luminescence at 525 nm has been monitored. The filling of the electron traps (excitation of the sample) was performed, unless otherwise specified, with the 254 nm line from a 200 W Hg lamp. In a few experiments excitation was produced by a pulsed excimer laser, i.e., the 248 nm output from KrF or the 308 nm output from XeCl.

The TSL spectra were obtained by raising the temperature of a previously excited sample using a homemade linear temperature scanner. The heating rates attainable were between 0.1 and 0.8 K/s, and the luminescence was detected by a GaAs photomultiplier-electrometer combination. An analogous system equipped with electronic shutters was used for studies of the decay of phosphorescence.

The PSL was induced by a nitrogen-pumped dye laser emitting pulses in the range of 50–200 μJ at wavelengths between 580 and 640 nm. The luminescence pulses were

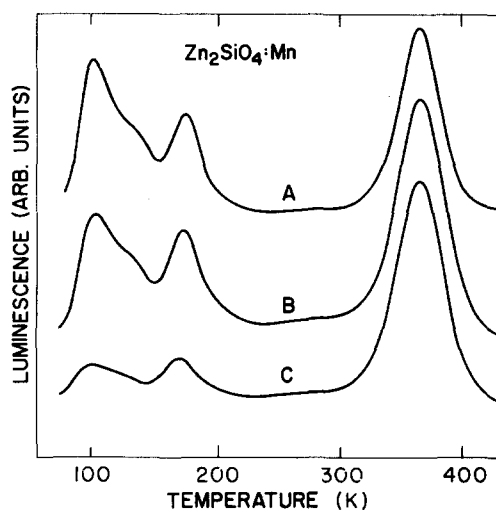


FIG. 1. Thermostimulated luminescence spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}$, (P1). The sample was cooled to 77 K, irradiated with ultraviolet light of wavelength λ for 5 min, and warmed at a uniform rate of 0.5 K/s—(A: $\lambda = 254$ nm, B: $\lambda = 313$ nm, C: $\lambda = 334$ nm).

detected with a combination of a 0.5 m monochromator, a GaAs photomultiplier, and a storage scope.

III. RESULTS AND DISCUSSION

A. Thermally stimulated luminescence

In our studies of the long-lived luminescence of these phosphors we have used TSL measurements to determine the characteristics of the electron trapping centers. By irradiating with ultraviolet light of wavelength $\lambda < 350$ nm (3.5 eV) we were able to fill some of the electron traps. When this was done at liquid nitrogen temperature and the temperature T was subsequently raised at a constant rate, $T = T_0 + \beta t$, we obtained the TSL spectra or "glow curves." Three such spectra taken from samples irradiated by light of different photon energies are shown in Fig. 1. In addition to providing evidence for several sets of trapping levels these spectra demonstrate that the relative populations of the levels depend on the photon energy used.

The TSL spectra can also provide estimates of the activation energies associated with the electron traps, if the recombination channel is known. To obtain these energies we have used a procedure introduced by Hoogenstraaten,¹⁵ which analyzes the shift of the TSL peaks with changes in the temperature scanning rate β . These peak positions are determined by a competition between the depletion of the traps and the increase with increasing temperature of the thermal excitation rate. We find that the tunneling rates are generally too small to explain the rapid drop in intensity observed at temperatures above the peaks in the spectra. Thus, although in the temperature range below a peak the tunneling process is the dominant recombination mechanism, at and above the peaks it is exceeded by diffusion of electrons released thermally into the conduction band. For this reason the Hoogenstraaten method, which was developed for a nontunneling recombination model, is found to apply

with reasonable accuracy for the tunneling model as well. One must keep in mind, however, that the *ionization* energies determined by this method may be slightly larger than the *excitation* energies which determine the tunneling recombination rates. This will be discussed further below.

To determine the energies one measure the temperatures (T_m) corresponding to the maxima of the TSL peaks as a function of the temperature scanning rate β ($T = T_0 + \beta t$). The slope of the curve $\ln(\beta/T_m^2)$ vs $1/T_m$ equals $-1/k$ times the activation energy E ,

$$\beta/T_m^2 \propto e^{-E/kT_m}.$$

A typical plot for the "360 K" system is shown in Fig. 2. In this way, the activation energies of the traps seen in Fig. 1 are determined to be 0.2, 0.25, 0.3, and 0.8 eV. (The weak maximum seen near 260 K apparently corresponds to the strong 0.6 eV peak measured in the P39 materials, see Fig. 4. This 260 K peak is the dominant one in TSL spectra from P1 samples manufactured by General Electric.) As noted above, the fact that Figs. 1 and 2 are consistent with the Hoogenstraaten analysis cannot be taken as proof that thermal detrapping of electrons to the conduction band is the sole channel responsible for recombination luminescence. As has already been pointed out by Kivits,¹⁶ other mechanisms, such as electron tunneling from thermally populated excited states of the traps, could yield analogous behavior.

If a distribution of trap levels exists, as has been proposed^{2,3} to explain the t^{-1} decay, it should appear directly in the TSL spectra as an anomalous linewidth. The peaks in the spectra in Fig. 1 are not markedly

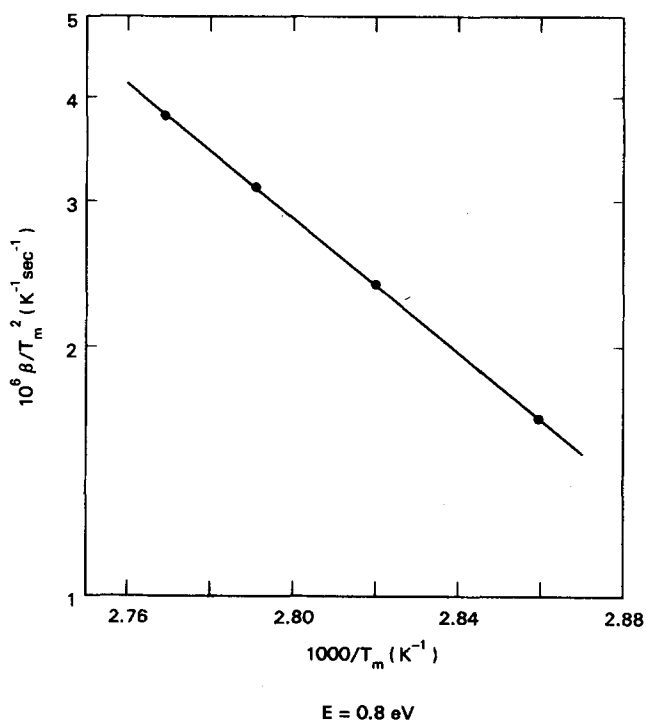


FIG. 2. A Hoogenstraaten plot for the 360 K trap system of a P1 phosphor; see Fig. 1. The slope determines the energy $E = 0.8$ eV.

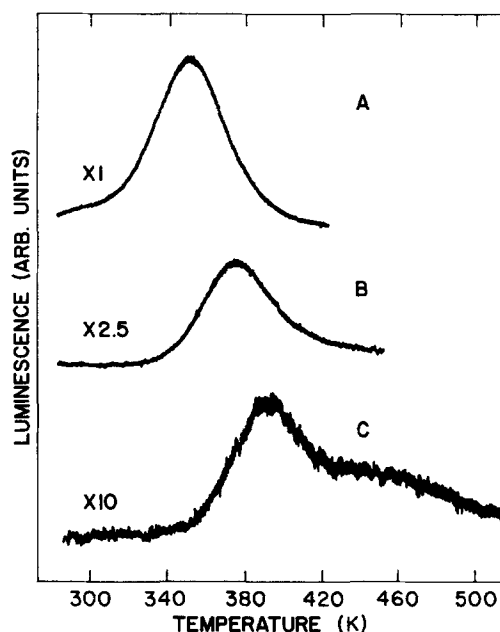


FIG. 3. Thermal hole burning in the 360 K (0.8 eV) peak of the phosphor shown in Fig. 1. The sample was irradiated with 254 nm light at 273 K, the excitation was removed and either (A) the sample was warmed at 0.5 K/s, (B) the sample was warmed at 0.5 K/s after being brought to 370 K and then cooled rapidly to 273 K, or (C) the sample was warmed at 0.5 K/s after being brought to 390 K and then cooled to 273 K.

different from those predicted by Kivits,¹⁶ which suggests that a more sensitive method is needed to detect any distribution of trap energies that may exist. We have probed this question using a procedure analogous to the "hole-burning" experiments performed on optical line shapes. This involves filling the electron traps at a low temperature, increasing the temperature up to a certain point (T_i) below the peak, cooling again to low temperature, and finally scanning the TSL spectrum. It is observed (Fig. 3) that as T_i is progressively increased, the temperature T_m at the maximum is raised, which suggests that each trap "level" consists of a distribution of levels whose shallower part has been depleted by thermal release of electrons at the temperature T_i . It is thus clear that even in cases where only a single peak is observed there may still be a distribution of occupied electron trap levels of differing depths, although the data suggest that its width is not over 0.1 eV. We return to this point below.

In Fig. 4, we show a TSL spectrum for a zinc silicate phosphor containing manganese and arsenic (P39). The most important effect of the arsenic is the introduction of a deep trap appearing as a peak at about 550 K. A Hoogenstraaten plot gives an activation energy of $E = 1.9$ eV. This deep trap can be interpreted as being due to the substitution of Si^{4+} by As^{5+} , thus creating a positive Coulomb trapping center. From a comparison of Figs. 1 and 4 it would appear that the arsenic doping has also eliminated the shallower traps and greatly enhanced the trap density around 260 K (0.6 eV). However, thermal annealing (20 h at 1500 K) of the sample (United States Radium P39) causes a reappearance of

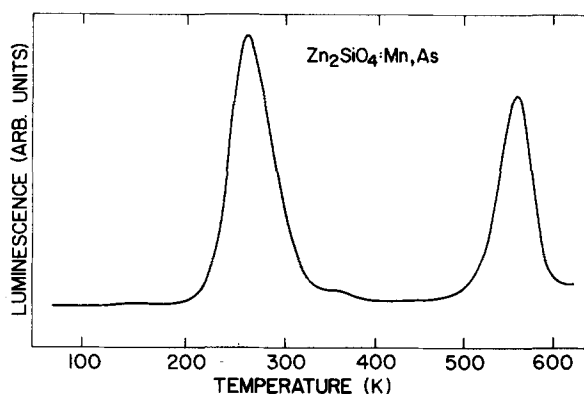


FIG. 4. Thermostimulated spectrum of $\text{Zn}_2\text{SiO}_4:\text{Mn, As}$ (P39) excited with the 254 nm/Hg line and heated at 0.5 K/s.

the shallow traps and a reduction in the number of those near 0.6 eV, though without seriously depleting the 1.9 eV traps. This fact indicates that it is not the chemical nature of arsenic that is responsible for the modification of the shallower traps but, more probably, the different treatment of the sample during its preparation. As noted above, quantitative differences with respect to trap densities have been observed among zinc silicate samples provided by different manufacturers.

B. Photostimulated luminescence

Light as well as heat can be used to release the trapped electrons and generate phosphorescence through electron-hole recombination. This is demonstrated by the fact that long wavelength light which is not absorbed by the Mn^{+2} centers still gives green Mn^{+2} emission from crystals whose traps have been previously filled. More explicit evidence of this fact appears in Fig. 5, where we show that 585 nm light can release electrons from the 260 K traps of the P1 samples and redistribute a small fraction (<10%) of these among the other traps (retrapping). By performing experiments analogous to those shown in Fig. 5 on the P39 samples we have found that only the electrons in the shallower traps—260 K (0.6 eV) and 360 K (0.8 eV)—can be photoexcited to any measurable degree by light of wavelength longer than the Mn^{+2} absorption threshold, ≈ 580 nm. Although the luminescence from the 360 K (0.8 eV) trap of the P1 phosphors was found to occur with nearly constant efficiency (within a factor of 3) when light of wavelength between 580 and 640 nm was used, the 950 nm output of an F-center laser (F_2^+ in NaF) gave, at the same power level, a very weak signal (at least two orders of magnitude lower than that produced at 585 nm).

Because the PSL signal is very weak when conventional cw light sources are used, we have excited the luminescence with a pulsed dye laser and measured the amplitudes of the emitted light pulses. To interpret these experiments we make two assumptions, which are found to be consistent with the data. (1) The dominant effect of the stimulating light is to excite some of the trapped electrons into excited "tunneling" states. (2) When the light is off the excited electrons relax rapidly back into their ground states. Assumption (1) postulates that any electrons which reach the conduction band are

captured into the excited trap states and neglects any possible effects of the redistribution or diffusion of the excited electrons. No effects attributable to either redistribution or diffusion have been identified. Assumption (2) is always satisfied unless the tunneling state is metastable. With these assumptions the pulsed experiments can be interpreted in the same way as the cw experiments, except that the lapsed time t is replaced by the time that the light is on. Thus, if there have been ν pulses of length δt each, the observed response is that produced at a time $t = \nu \delta t$. Hence, we show the time decay of PSL in a plot of the amplitude of the luminescence pulse (or its reciprocal) versus the number ν of laser pulses. In a test of linearity we found that the PSL signal observed at 525 nm was always linearly dependent on the dye laser intensity.

C. Time dependence of luminescence

In Figs. 6 and 7 we show two typical phosphorescence and PSL decay curves plotted as $(\text{intensity})^{-1}$ versus either time t or the number ν of laser pulses. The relationship is seen to be very close to a linear one (except near $t=0$), and the fact that *both* curves decay approximately as t^{-1} has very important implications in the choice of an acceptable recombination model. As mentioned in the Introduction, a widely accepted explanation of a t^{-1} decay involves traps distributed over a wide range of energy. The decay of such a distribution consists of a sum of simple exponential decays, each determined by the thermal detrapping rate [$k = S \exp(-E/kT)$] appropriate to the energy E of some fraction of the traps. In a PSL experiment, however, the detrapping rate is determined by the light intensity and not by thermal activation, and a distribution of electron traps cannot explain the t^{-1} decay. Thus, even though our thermal hole-burning experiment, Fig. 3, suggests that a narrow (≈ 0.1 eV) distribution of trap energies occurs, this

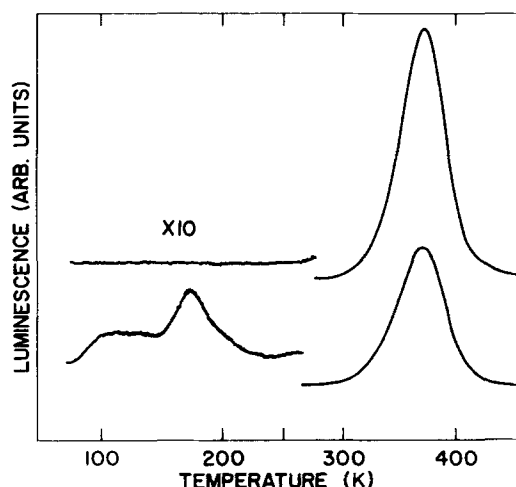


FIG. 5. Retrapping of photoexcited electrons in the 360 K (0.8 eV) trap system of a P1 sample. Top: The spectrum obtained by irradiating at 295 K, cooling rapidly to 77 K, and then increasing the temperature at 0.5 K/s. Bottom: As above, but with the sample exposed to 590 nm light for 20 min while at 77 K.

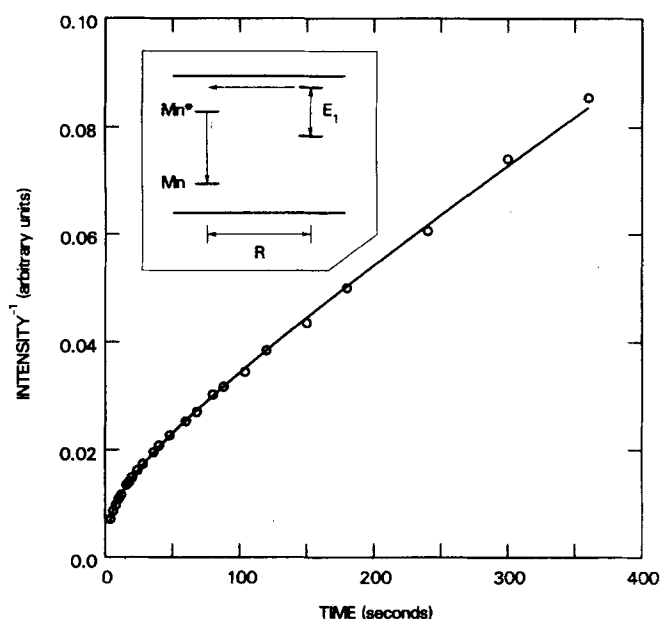


FIG. 6. Phosphorescence decay curve of a P1 sample at 323 K. The data are plotted as $(\text{intensity})^{-1}$ versus time and the solid line corresponds to Eq. (12) with $\eta = 0.00574 \text{ s}^{-1}$. The sample was irradiated for 20 min with 254 nm light. Insert: A schematic diagram of the ground and excited bound state energy levels of an impurity pair—manganese on the left and a deep trap on the right. Tunneling from the shallow excited trap state into the excited Mn^* state and the subsequent radiative decay are indicated by the arrows into and out of the Mn^* level.

distribution cannot explain the PSL experiment and is, also, probably not broad enough to explain the t^{-1} decay of phosphorescence as well.

In the following sections we develop a model based on electron tunneling to account for the t^{-1} decay of both phosphorescence and PSL. It was pointed out that the decay deviates from t^{-1} , especially at early times. We shall show that our model accounts for these discrepancies and provides a more general expression which is followed at all times.

IV. TUNNELING THEORY

A. The model

In this section we develop a general theory of pair recombination (tunneling) as it applies to phosphors. We assume that the light is emitted by excited activator ions, manganese in the present example, when they decay to their ground state. These excited ions are produced by capture of electrons on Mn ions which have been given a net positive charge, relative to the host crystal, either by direct photoionization with ultraviolet light or by capture of photoexcited holes. (The excitation could also be generated electrically.) The capture process is assumed to proceed by tunneling from the nearest shallow electron trap, which we call a "donor." Thus, the Mn ions and donors can be thought of as pairs whose distribution (both in space throughout the crystals and as a function of pair separation R) has been grown in during the preparation of the material. Direct recombination between Mn ions and free electrons is neglected

so that, as noted above, the theory may not apply on the high temperature side of the glow peaks.

The essential property of a donor is that it be shallow and have, hence, a wave function which can overlap measurably any nearby Mn ion. As this property is shared with excited states of deep electron traps, we shall include the latter (and, thus, essentially all traps) in the class of donors. It is expected that electrons (and, to a lesser extent, holes) will have a limited mobility in the conduction (or valence) band, so that it is possible for the charges to be transferred from one trapping center to another. (This is confirmed by the "retrapping" experiments of Fig. 5.) In the analysis which follows, however, we shall ignore this possibility and assume that an electron released, either optically or thermally, from a trap will be recaptured on the same trap. In most experiments the difference would not be detectable. An exception occurs, however, as we noted previously, at temperatures above the glow curve peaks, where tunneling is not the dominant recombination mechanism.

We develop the model with the convenient restriction that (at most) two states are available to the trapped electron—one shallow tunneling state and also, if the traps are deep, one localized state. The extension to include a sum over many excited states is found not to alter the results significantly and will be omitted.

Schematic diagrams of the luminescence mechanisms appear as inserts in Figs. 6 and 7. After excitation with ultraviolet light an electron has been removed from a manganese ion (shown on the left) and an electron (not

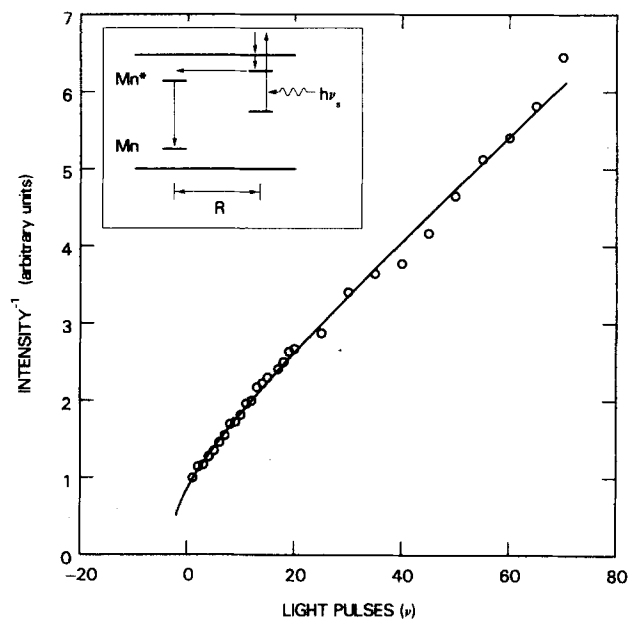


FIG. 7. Photostimulated luminescence decay curve for a P1 sample at 295 K plotted as $(\text{intensity})^{-1}$ versus number of 635 nm dye laser pulses applied, $\delta t \approx 5 \text{ ns}$. The solid curve is Eq. (17a) with $\eta \delta t = 0.0346$ and $t_2 = 2.5 \delta t$. The sample was irradiated for 5 min with 254 nm light. Insert: A schematic diagram of the processes leading to PSL—photoexcitation (and subsequent capture into the excited trap level), tunneling, and radiative recombination.

necessarily the same one) has been captured in a nearby deep trap state (shown on the right). This trapped electron, when excited either thermally (Fig. 6) or optically (Fig. 7) into its shallow tunneling state, can tunnel the distance R to the nearby manganese ion and be captured into the excited Mn^* state. The luminescence occurs when this excited state decays radiatively to the ground state Mn .

In the present analysis we shall treat only a single species of trap and derive results which can then be summed over species as needed for each experiment. Thus, we let $P(R)dR$ be the number of the donor-manganese pairs being considered which have a separation between R and $R+dR$ and let $p(R)dR$ be the number of these which have captured holes on the manganese, as we discuss in Sec. IV C below. The latter decay radiatively by tunneling of electrons from the donors at a rate,

$$W(R) = W_0 e^{-2R/a}, \quad (1a)$$

where a is the effective radius for overlap of donor wave functions with the manganese, and the coefficient

$$W_0 = \Omega \rho(T, I) = \Omega n^t / n \quad (1b)$$

is proportional to the fraction ρ of (paired) trapping centers in their tunneling states. The number n^t of tunneling pairs, although it includes all pairs ($n^t = n$) for the most shallow traps will depend, in general, on the temperature T and on the intensity I of any exciting light which is present—see Eq. (14c). The decay rate of the pairs, is thus,

$$\dot{p}(R) = -p(R) W(R). \quad (2a)$$

Expression (2a), when summed (integrated) over R , determines both the decay rate of p the total number of pairs and the intensity L (in photons per second) of the light they emit,

$$L = -\dot{p} = - \int_0^\infty dR \dot{p}(R) = \int_0^\infty dR p(R) W(R). \quad (2b)$$

The quotient of Eqs. (2a) and (2b) yields the time-independent equation

$$\frac{dp(R)}{dp} = \frac{p(R) W(R)}{\int_0^\infty dR' p(R') W(R')} = \frac{p(R) e^{-2R/a}}{\int_0^\infty dR' p(R') e^{-2R'/a}}, \quad (2c)$$

which shows that (for each type of pair) the distribution $p(R)$ at any time is determined uniquely by the initial distribution after charging is ended and by the total number of pairs which have subsequently recombined. This is an important result, as it greatly simplifies the interpretation of the more complex experiments employing changing experimental conditions—as in “photo-stimulation,” described below.

B. The $1/t$ law

For any species of pair the decay coefficient $W(R)$ is time independent and $p_0(R)$, the density of pairs at $t=0$, becomes at times t ,

$$p(R) = p_0(R) \exp[-W(R)t], \quad (3)$$

so that the total light intensity L from the decay of all pairs is

$$L = \int_0^\infty dR p_0(R) W(R) \exp[-W(R)t]. \quad (4)$$

To evaluate Eq. (4), we set

$$u(R) = W(R)t \leq u_{\max} \equiv W_0 t, \quad (5a)$$

so that

$$du = d(Wt) = -(2/a) u dR \quad (5b)$$

and

$$L = \frac{a}{2t} \int_0^{u_{\max}} du p_0(R) \exp(-u). \quad (6)$$

As $p_0(R)$ is normally a slowly varying function of u , we may replace it by its mean value \bar{p}_0 (independent of u or R). In addition, the upper limit $u_{\max} = W_0 t$ may usually be replaced by ∞ , so that the integral in Eq. (6) is easily evaluated and gives the hyperbolic result

$$L \approx a \bar{p}_0 / 2t \propto 1/t. \quad (7)$$

C. The initial pair distribution

The initial pair density $p_0(R)$ is determined by both the distribution of paired impurities $P(R)$ in the sample and the mode of excitation used to populate them. If the manganese and donor impurities are distributed at random in the materials, then the number of pairs $P(R)dR$ of separation between R and $R+dR$ is proportional to the volume $4\pi R^2 dR$ available to a donor in this range of distances from a manganese ion. If the density of impurities is large, this should be multiplied by a “nearest-neighbor factor,” the probability that there is no donor closer than the one at R .⁵ This factor is normally unimportant for the close pairs which produce the luminescence, but is important in counting the total number of pairs. Its effect can be approximated by introduction of an effective cutoff in the R integration, $R < R_{\max}$.

Normally the pairs are excited by ultraviolet light which irradiates the sample for some time, say, t_1 . In this case the initial excited pair distribution $p_0(R)$ at the start of phosphorescent decay is produced by a competition between the preceding excitation and decay processes. We assume that the pair excitation rate is proportional to the ultraviolet light intensity I_1 with proportionality constant α_p , so that the rate equation becomes

$$\dot{p}(R) = \alpha_p I_1 [P(R) - p(R)] - W'(R) p(R). \quad (8)$$

Here the prime in W' is to remind us that this quantity may depend on I_1 through changes in the population of the tunneling levels. Equation (8) has the solution

$$p(R) = \alpha_p I_1 \tau'(R) P(R) \{1 - \exp[-t_1/\tau'(R)]\}, \quad (9a)$$

where the lifetime,

$$\tau'(R) = [\alpha_p I_1 + W'(R)]^{-1}, \quad (9b)$$

contains a dependence on both I_1 and R . Equation (9a) shows that as t_1 becomes large compared to $\tau'(R)$, $p_0(R)$ approaches the steady state value

$$p_0(R) = \alpha_p I_1 \tau'(R) P(R) = \frac{\alpha_p I_1 P(R)}{\alpha_p I_1 + W'(R)}, \quad (10)$$

but at a rate which depends on I_1 and differs for pairs of

differing R . The distant pairs respond most slowly and, as these are the most numerous, they determine the time required for the system to stabilize. Thus, the steady state values are given by Eq. (10), but the times required for these to be attained for all pairs are determined by $\tau'(R)$ from Eq. (9b) with $R \approx R_{\max}$.

D. A general solution

In most cases, an expression for the decay of luminescence can be derived which spans both high and low intensities. By using Eq. (10) we can rewrite Eq. (6) as

$$L = \frac{a}{2} \eta \int_0^{u_{\max}} du P(R) \frac{e^{-u}}{u + \eta t}, \quad (11a)$$

where we have introduced a new parameter η which contains the dependence on I_1 . We define this parameter by

$$\eta = \alpha_p I_1 / \gamma_1(I_1), \quad (11b)$$

where γ_1 describes the intensity dependence of $W'(R)$,

$$\gamma_1(I_1) = W'(R)/W(R) = W'_0/W_0, \quad (11c)$$

and is discussed below, see Eq. (15a). If $P(R)$ is replaced by its mean value \bar{P} for $R < R_{\max}$ ($u > u_{\min}$), Eq. (11a) becomes¹⁷

$$L = \frac{a}{2} \eta \bar{P} \int_{u_{\min}}^{u_{\max}} du \frac{e^{-u}}{u + \eta t} \approx \frac{a}{2} \bar{P} \eta e^{\eta t} E_1(\eta t), \quad (12)$$

where, in the final expression, u_{\min} and u_{\max} have been replaced by zero and infinity, respectively. In this result the exponential integral function can be evaluated as the sum¹⁷

$$E_1(u) = \int_u^\infty \frac{dt}{t} e^{-t} = -\ln(\gamma u) - \sum_{\nu=1}^\infty \frac{(-u)^\nu}{\nu \nu!} \quad (13a)$$

with $\gamma = 1.78107$ or as the continued fraction¹⁷

$$E_1(u) = e^{-u} / [u + g_1(u)] \quad (13b)$$

with

$$g_\nu(u) = \nu / \{1 + \nu / [u + g_{\nu+1}(u)]\}, \quad \nu = 1, 2, \dots \quad (13c)$$

The sum converges very rapidly for small arguments and the continued fraction for large. Equation (12) is the desired result. It shows that to a good approximation the emission intensity is proportional to a one-parameter function of the time. We shall find below that the same function describes the decay of photostimulated emission.

It is easily shown that, except at very small times, \bar{P} is nearly independent of time. Further, if ηt becomes much larger than unity, Eq. (12) reduces approximately to

$$L \propto 1/(t + \eta^{-1})$$

as is observed. It is significant to note that under conditions of strong illumination, as with intense ultraviolet light, the coefficient γ_1 can become proportional to the intensity, so that η is constant and the emission intensity Eq. (12) saturates, becoming independent of I_1 .

E. The population of the tunneling states

In order to determine the dependence of the parameter η on temperature and excitation intensity, we must derive expressions for the number of electrons which are excited into the tunneling states. We consider a trap which has a single nondegenerate tunneling level at an energy E above its ground state. The relevant quantity, the fraction $\rho(T, I_1)$ of the pairs which have their electrons in this state, is determined by the rate equation

$$\dot{n} = 0 = c_1 n_1 - (e_1 + \alpha_1 I_1)(n - n_1), \quad (14a)$$

where n is the total number of electrons and n_1 is the number in the tunneling state. For transitions between the two states, $c_1 n_1$ describes capture into the ground state, while $(e_1 + \alpha_1 I_1)(n - n_1)$ describes the effective thermal and optical excitation up into the excited state. The two coefficients c_1 and e_1 are easily shown by detailed balance to be related,

$$e_1 = c_1 e^{-x}, \quad (14b)$$

where any degeneracy factors have been omitted and

$$x = E/kT.$$

Hence, we find for the occupancy factor, Eq. (1b),

$$\rho(T, I_1) = \frac{n_1}{n} = \frac{e_1 + \alpha_1 I_1}{c_1 + e_1 + \alpha_1 I_1} = \frac{e^{-x} + \alpha_1 I_1 / c_1}{1 + e^{-x} + \alpha_1 I_1 / c_1}. \quad (14c)$$

Equations (14) can be used to evaluate the coefficients γ_1 and η introduced in Eqs. (11) above. Thus

$$\gamma_1(I_1) = n_1(I_1)/n_1(0) = [1 + e^x] / \left[1 + \left(\frac{\alpha_1 I_1}{c_1} + e^{-x} \right)^{-1} \right] \quad (15a)$$

and, if e^{-x} is much less than unity we find

$$\eta = \alpha_p \left(I_1 + \left[\frac{\alpha_1}{c_1} + \frac{e^{-x}}{I_1} \right]^{-1} \right) e^{-x}. \quad (15b)$$

If, further, $\alpha_1 I_1 / c_1 \gg e^{-x}$, then Eq. (15b) reduces to the useful expression

$$\eta = \alpha_p (I_1 + c_1 / \alpha_1) e^{-x}. \quad (15c)$$

F. Photostimulation

As noted above, the PSL experiment studies recombination of the electrons excited optically into the tunneling levels of the deep traps (see the insert in Fig. 7) after the electrons excited thermally from the shallower traps have recombined. We let n_2 be the number of the latter electrons (and of the corresponding pairs). As a consequence of Eq. (2c) the resulting pair distribution, though more complex than Eq. (10), depends only on the starting distribution and on the number of pairs n_2 . Hence, the decay of the luminescence is again given by Eq. (11a) though with the time displaced by an amount t_2 , which is just the time which would have been required for the n_2 pairs annihilated by the electrons in the shallower traps to recombine under the conditions of the photostimulation experiment.

To derive the desired expressions we assume that the

fraction of electrons in the tunneling states is determined by Eq. (14c) while the light is on but are quickly retrapped when the light is off. (Retrapping by the thermally unstable shallow traps can be ignored.) Consequently, the recombination rate under illumination of intensity I is determined by

$$W(R) = \Omega \rho(T, I) e^{-2R/a}. \quad (16a)$$

Also $p_0(R)$ is given by Eq. (10) with

$$W'(R) = \gamma_t W(R), \quad (16b)$$

where

$$\gamma_t = [\rho(T, I_1)/\rho(T, I)], \quad (16c)$$

and the resulting light intensity is again given by Eq. (12) though with γ_1 , Eq. (11c), replaced by γ_t . Hence, the luminescence follows

$$L(t) = (a/2)\eta\bar{P} \exp[\eta(t+t_2)] E_1[\eta(t+t_2)] \quad (17a)$$

with

$$\eta = \alpha_p I_1 / \gamma_t, \quad (17b)$$

except for very small t , and in the pulsed experiments ηt translates into $\nu \eta \delta t$ for ν light pulses of length δt each. In Eq. (17a) the time displacement t_2 is related to the number of recombined pairs n_2 through

$$n_2 = \int_{-t_2}^0 L(t) dt = \frac{a}{2} \bar{P} [e^{\eta t_2} E_1(\eta t_2) + \ln(\gamma \eta t_2)], \quad (17c)$$

where, again, $\gamma = 1.78107$.

G. Comparison with experiment

The results derived above are compared with experiment in Figs. 6–9. The solid curves drawn in Figs.

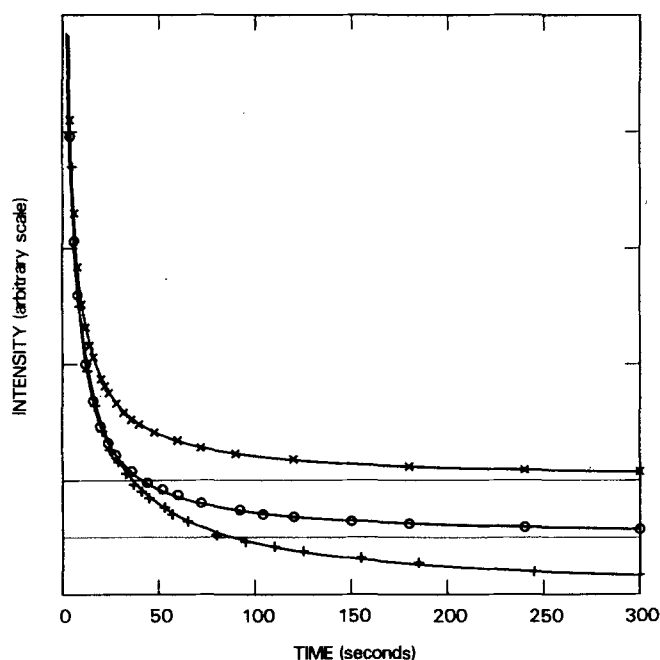


FIG. 8. The decay of phosphorescence from a P1 sample at three temperatures: (+) 323 K, (O) 273 K, and (x) 223 K. The solid lines correspond to Eq. (12) with $\eta = 0.033$, 0.317 , and 0.104 s^{-1} , respectively. The second and third curves have been displaced upwards for clarity.

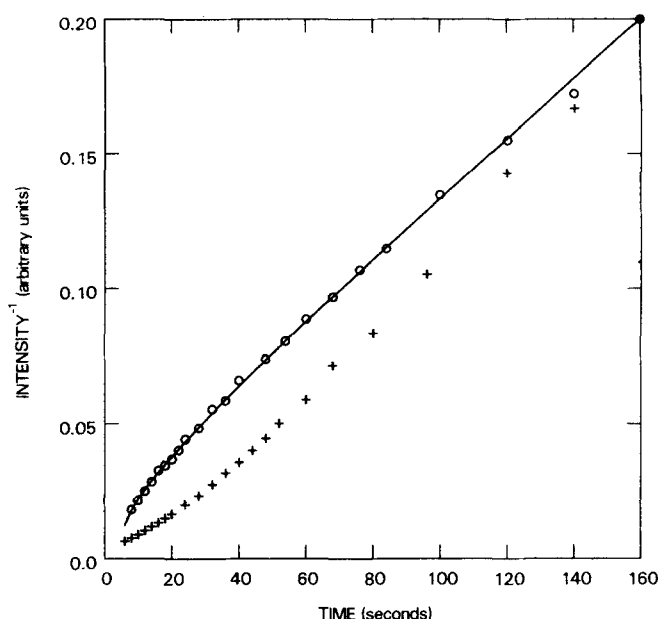


FIG. 9. The decay of phosphorescence from a P39 sample at two temperatures: (O) 423 K and (+) 298 K. The solid line corresponds to Eq. (12) with $\eta = 0.028 \text{ s}^{-1}$.

6 and 7 correspond, respectively, to Eq. (12) with $\eta = 0.00574 \text{ s}^{-1}$ and to Eq. (17a) with $\eta \delta t = 0.0346$ and $t_2 = 2.5 \delta t$, and both are found to agree with the data within a few percent. The values of η were chosen as those values for which a least squares fit of the data to

$$\ln[L(t)] = C + m \ln\{\exp[\eta(t+t_2)] E_1[\eta(t+t_2)]\} \quad (18)$$

gave $m=1$. The value of t_2 was chosen, where appropriate, to minimize the rms error in the fit of $\ln[L(t)]$ to the right-hand side of Eq. (18). Figure 8 shows similar fits of Eq. (12) to intensity versus time curves for a P1 sample studied at three temperatures, 323, 273, and 223 K. The corresponding values of η were 0.033 , 0.317 , and 0.104 s^{-1} .

As a further test of the model the experiments from which Fig. 8 was drawn were repeated with the exciting intensity I_1 reduced by a factor of 10. Correspondingly good fits to Eq. (12) were obtained, but the values of the parameter η were reduced at all three temperatures by a factor of only 3.0, indicating partial saturation of the excitation; see Eq. (15c). These results taken together with Eqs. (11) and (15c) yield the following relationships. (1) The full intensity (as for Fig. 8) is $I_1 = 2.9c_1/\alpha_1$ independent of temperature. Hence, (2) $\eta e^x = 3.9\alpha_p c_1/\alpha_1$ is a constant and the factors e^{-x} for the traps which feed the luminescence at the three temperatures satisfy $e^{-x} \propto 1, 9.6, 3.15$ for $T = 323, 273$, and 223 K , respectively. Since the high temperature emission must be dominated by the $E = 0.8 \text{ eV}$ (360 K) trap, these values determine the exponential factors:

$$e^{-x} = 3.33 \times 10^{-13}, \quad 3.20 \times 10^{-12}, \quad 1.05 \times 10^{-10};$$

and yield for the trap energies

$$E = 0.8, \quad 0.62, \quad 0.53 \text{ eV}.$$

This calculation also determines the quantity $\alpha_p c_1/\alpha_1 = 2.54 \times 10^{10} \text{ s}^{-1}$. The two lower energies, which probably

correspond to a single species of trap, can be identified with the strong 0.6 eV peak near 260 K shown in Fig. 4 for a P39 sample, which is also present, though weak, in Fig. 1. Note, however, that, if the excitation energy E into the tunneling state is less than the measured ionization energy of 0.8 eV for the 323 K trap, the excitation energies of the two more shallow states would be proportionately reduced.

Phosphorescence data obtained from a P39 sample at two temperatures are shown in Fig. 9. The data for the upper curve were taken at 423 K, where only the high temperature (550 K or 1.9 eV) trap is stable, and are fit very well by Eq. (12) with $\eta = 0.028 \text{ s}^{-1}$. The lower curve, which was obtained at 298 K on the *high* temperature side of the 260 K peak, has a very different shape and cannot be fit by Eq. (12). It does, however, fit the expression $L \propto [e^{\eta t} E_1(\eta t)]^2$ with $\eta = 0.011 \text{ s}^{-1}$, which supports the suggestion, made above, that the recombination mechanism on the high temperature side of the peaks may include a significant bimolecular part.

V. SUMMARY

We have presented luminescence data for manganese-doped zinc silicate phosphors and have shown that they are *inconsistent* with the accepted model based on a distribution of trap energy levels. The data are in excellent agreement, however, with a pair recombination (tunneling) model whose parameters are found to depend principally on the response of the pairs to the exciting ultraviolet light. The model leads to a simple expression of light intensity versus time which agrees with the experimental data for persistent luminescence excited either thermally (phosphorescence and TSL) or optically (PSL).

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