

An explanation of the power-law decay of luminescence

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 1359

(<http://iopscience.iop.org/0953-8984/18/4/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 08:52

Please note that [terms and conditions apply](#).

An explanation of the power-law decay of luminescence

D J Huntley

Department of Physics, Simon Fraser University, Burnaby, BC, V5A 1S6, Canada

Received 14 October 2005, in final form 14 November 2005

Published 13 January 2006

Online at stacks.iop.org/JPhysCM/18/1359

Abstract

Luminescence decay with time often shows a power-law dependence of the form intensity $I \propto t^{-k}$, where t is time and k is usually in the range 1–1.5. It is shown here that this power law can result from the tunnelling of trapped electrons to recombination centres that are randomly distributed, and that the range of exponents matches that of the observations. The explanation accounts for the most extreme case of an observed $t^{-1.06}$ dependence extending over nine decades of time.

1. Introduction

Luminescence is the light emitted by matter in response to a stimulus or excitation. As expected, the intensity normally decreases with time after the excitation, but the form of the decay is not always well understood. The latest comprehensive review of the topic appears to be that of Jonscher and de Polignac (1984). They note that when, after excitation, the electron becomes trapped at a defect, the decay often follows a power law of the form intensity $I \propto t^{-k}$, where t is time and k is a constant which is usually between 1 and 1.5, but can be less than 1 and as high as 2. The power-law decay is observed over 3–4 decades of time, though in one case it covers nine decades.

An exponential decay is expected for the case of thermal excitation from a set of identical traps. Non-exponential decays can arise from thermal excitation of electrons from traps when there is a distribution of traps; in particular, a power-law decay results when the distribution is exponential in energy (Randall and Wilkins 1945; Chen and Kirsch 1981, see also, p. 172). Non-exponential decays can also result when retrapping occurs during optical excitation of electrons from traps (McKeever *et al* 1997, Chen and Leung 2003), but it seems unlikely that models of this kind can account for an extended power-law decay. Jonscher and de Polignac (1984) attempted to fill the gap with a general theory, but did not offer a specific mechanism. Klik and Chang (1993) pointed out that ‘Ever since the pioneering work of Street and Wolley (sic) (1949, 1952, 1956) and Gaunt (1976, 1986) it has been recognized that logarithmic relaxation arises in composite systems as an average (net) evolution law for a large number of

exponentially decaying individual components'; the proposal described below can be regarded as being in this category.

The theory proposed here is based on the tunnelling of electrons from traps to recombination centres; it provides an explanation for extended power-law decay with non-integral exponents both smaller and larger than 1, and in particular can explain the observed $t^{-1.06}$ decay over nine decades of time. Although tunnelling was considered as an explanation earlier (e.g. Thomas *et al* 1965, Riehl 1970, Delbecq *et al* 1974, Avouris and Morgan 1981) the simple theory given here has not been proposed.

Our interest in the topic arises from a desire to understand the processes occurring in feldspars that permit optical dating (Aitken 1998); phosphorescence after ionizing radiation or illumination is observed to decay as a power law (Visocekas 2002, Baril and Huntley 2003, Baril 2002), and the decay of optically excited luminescence shows power-law behaviour (Bailiff and Poolton 1991, Bailiff and Barnett 1994, Baril and Huntley 2003).

2. Theory

The assumptions are:

- (1) There are defects in the crystal that are traps for electrons. There are electrons in some of these traps as a result of an excitation pulse. No assumptions are necessary about their distribution.
- (2) There are other defects in the crystal to which an electron can tunnel from a trap and these are randomly distributed. Their density is much higher than that of the trapped electrons, so their density is effectively constant. These centres will be referred to as recombination centres, and their density will be denoted by ρ .
- (3) The tunnelling of an electron to a nearby recombination centre is a random process with a mean lifetime, τ , given by the standard formula for tunnelling through a potential barrier of constant potential

$$\tau = s^{-1} e^{\alpha r} \quad (1)$$

where s can be thought of as an attempt-to-escape frequency, r is the tunnelling distance, and α is a constant (Thomas *et al* 1965, Riehl 1970). For an electron in an atom-sized box, $s \approx 3 \times 10^{15} \text{ s}^{-1}$.

- (4) An electron tunnels to the nearest recombination centre only. The rapid increase of τ with r makes the error introduced by this assumption insignificant.

The probability that there are no recombination centres in a volume V is $e^{-\rho V}$; thus the probability that there is no recombination centre within a distance r of a trap is

$$\exp\{-4\pi\rho r^3/3\} = \exp\{-(r')^3\}$$

where r' is a dimensionless variable defined by

$$r' \equiv \{4\pi\rho/3\}^{1/3} r. \quad (2)$$

The probability that the nearest recombination centre lies at a distance between r' and $r' + dr'$ is

$$p(r') dr' = 3(r')^2 \exp\{-(r')^3\} dr'. \quad (3)$$

The distribution $p(r')$ is shown by the bold curve in figure 1.

The number of trapped electrons remaining after a time, t , is found by integrating the probability of the nearest recombination centre being at a distance r multiplied by the

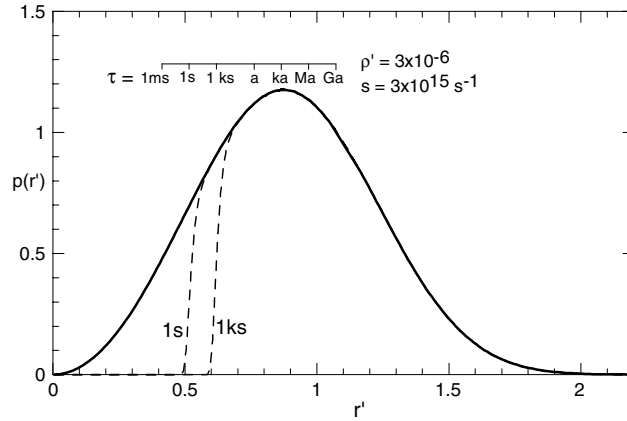


Figure 1. The solid line is the probability distribution of distances between trapped electrons and the nearest recombination centres in terms of the dimensionless variable r' , after an excitation pulse. The mean lifetime of the electrons is shown in the upper scale for the particular s and recombination centre density indicated; ρ' is the dimensionless recombination centre density and is defined in equation (5). The distributions of trapped electrons after 1 s and 1000 s are shown by the dashed lines; these are essentially coincident with the solid line at large values of r' . The fraction of electrons still trapped at a given time is given by the area under a dashed line.

probability that tunnelling has not occurred, $\exp(-t/\tau)$. Thus, using n to represent the trapped electron population, and n_i its initial value,

$$\frac{n(t)}{n_i} = \int_0^{\infty} 3(r')^2 \exp[-(r')^3] \exp(-t/\tau) dr'. \quad (4)$$

Note that τ depends on r' through equations (1) and (2).

The left dashed line of figure 1 shows the integrand at 1 s after a pulse excitation for a particular density of recombination centres. Notice that for $r' < 0.47$ essentially all the trapped electrons have tunneled out, while for $r' > 0.57$ only a small fraction of the trapped electrons have tunneled out. The right dashed line in figure 1 shows the integrand at 1 ks. It is important to notice that as time progresses this dashed line, representing the boundary of the trapped electron population, moves to the right, and that this occurs linearly on a logarithmic timescale. This is because equal changes in r' yield equal changes in $\log(\tau)$ (see equation (1)). If for those traps for which tunnelling is significant $p(r')$ is roughly constant, a good approximation to the integral, equation (4), is that n decreases linearly with $\log(t)$. The luminescence intensity is proportional to $-dn/dt$ and hence proportional to t^{-1} . This can be derived formally by noting that the luminescence intensity is proportional to the time derivative of equation (4), putting the $p(r')$ terms outside the integral, and integrating (see Avouris and Morgan 1981, for details). This approximation will be particularly good if the relevant electrons are at the peak of the $p(r')$ distribution, and can readily explain a t^{-1} dependence observed experimentally. If the tunnelling electrons are those with a tunnelling distance to the left of the peak of the $p(r')$ distribution, where $p(r')$ is increasing, then the intensity will increase with time relative to t^{-1} , thus an exponent >-1 is expected. Likewise if the tunnelling electrons are those with a tunnelling distance to the right of the peak, then an exponent <-1 is expected. What is not obvious is that in these situations the decay may follow a power law, and this will be shown.

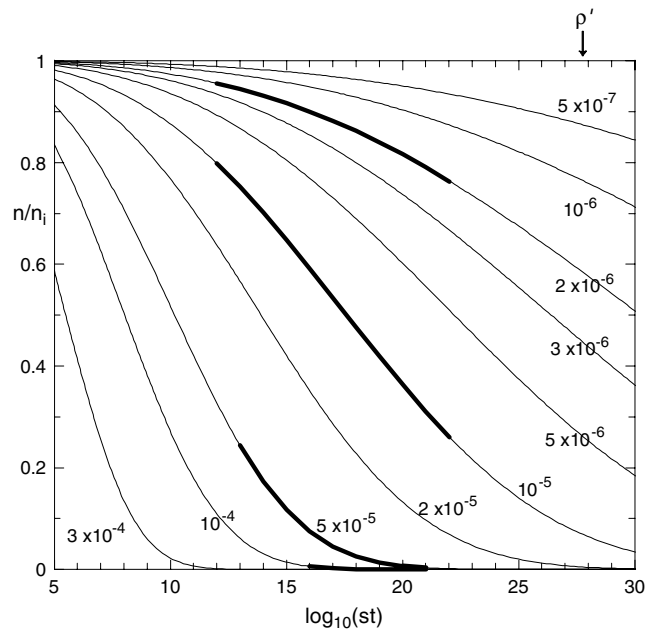


Figure 2. The number of electrons remaining trapped as a function of time. The different curves are for different densities of recombination centres, evaluated using equation (4). The upper two bold lines cover the period ~ 1 ms to ~ 1 month if $s = 3 \times 10^{15} \text{ s}^{-1}$.

It is convenient at this point to introduce the dimensionless variable ρ' for the density of recombination centres, defined by

$$\rho' \equiv \frac{4\pi\rho}{3\alpha^3} \quad (5)$$

where ρ' is the number of recombination centres within a sphere of radius α^{-1} . Plots of n/n_i versus $\log(st)$ are shown in figure 2 for several values of ρ' . These were obtained by evaluating the integral in equation (4).

A considerable simplification of the mathematics of equation (4) can be made using the following argument. Consider those trapped electrons with a particular electron–recombination centre distance; for times very much shorter than the mean life no significant tunnelling has occurred, while for times very much longer than the mean life nearly all the electrons have tunneled out. The approximation to be made is that for $t < \tau$ no tunnelling has occurred, while for $t > \tau$ all electrons have tunneled out; this approximation is justified because it is the logarithm of time that is the important variable, and corresponds to replacing the dashed lines in figure 1 by vertical lines. The critical tunnelling distance for a time, t , is thus from equation (1)

$$r_c = \alpha^{-1} \ln[st] \quad st > 1. \quad (6)$$

For trapped electrons for which the nearest recombination centre is closer than this distance, tunnelling will have occurred, and for all others tunnelling will not have occurred. As t increases, more and more electrons will have tunneled to nearby recombination centres. With this approximation the trapped electron density, n , will be given by the density of those without a recombination centre within a sphere of radius r_c ; thus

$$\frac{n}{n_i} = \exp\{-\rho'[\ln(st)]^3\}. \quad (7)$$

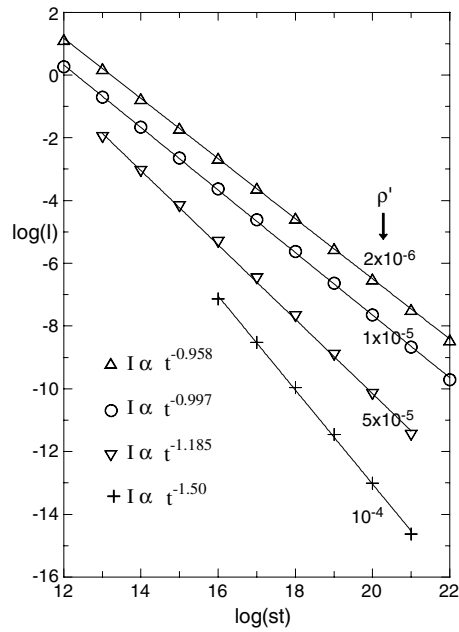


Figure 3. Log[intensity = $-(1/n_i) \, dn/dt$] versus log(time) for the four regions of the decay curves shown in bold in figure 2. The points were calculated by differentiating equation (4), although use of equation (8) makes a barely perceptible difference. The solid lines are linear fits to these points and the exponents obtained are shown on the graph. It is seen that a power law is a good fit for all. Except for the uppermost set, the data have been shifted vertically for clarity.

A comparison of the integral in equation (4) and the approximation of equation (7) shows good agreement, and that agreement to better than 5% can be obtained over nearly all of the region shown in figure 2 by replacing st in equation (7) by $1.8st$.

The luminescence intensity, I , is proportional to the rate of decrease of n with time. This can be obtained by differentiating equation (4), or by differentiating equation (7); the latter yields

$$I \propto -\frac{1}{n_i} \frac{dn}{dt} = 3\rho' t^{-1} [\ln(st)]^2 \exp\{-\rho' [\ln(st)]^3\}. \tag{8}$$

Some log–log plots of $(1/n_i) \cdot dn/dt$ versus st are shown in figure 3. These were obtained by differentiating equation (4), but the difference using equation (8) is barely discernible (the differences in $\log(I)$ are all <0.06 for the points of figure 3). These plots are very close to being linear and thus the relation between intensity and time follows a power law. The exponents for linear fits to the points are given on the figure. For $\rho' = 1 \times 10^{-5}$ a fit to the points calculated from equation (4) yields $I \propto t^{-0.997}$ accurately over ten orders of magnitude of time. For the examples shown in figure 3 the exponents range from -0.958 to -1.50 . For values of ρ' smaller than 2×10^{-6} the exponent approaches a limit of about -0.95 . For values of ρ' larger than 10^{-4} a power law becomes an increasingly poor fit, with exponents becoming rapidly increasingly negative.

3. Discussion

The power-law decay is of course an approximation to an exact solution, but a very good approximation (figure 3), and it is not surprising that experimental data are interpreted as showing a power-law decay. Outside the region shown in figure 3 the power law becomes an

increasingly poor fit, and in concurrence some of the experimental data reviewed by Jonscher and de Polignac show departures from the power law outside the power-law region.

The theory makes sense quantitatively. For example, assume that the tunnelling barrier is $E = 3$ eV; then $\alpha = 9 \times 10^9 \text{ m}^{-1}$. If $\rho = 5 \times 10^{17} \text{ cm}^{-3}$, then $\rho' = 3 \times 10^{-6}$, and for a tunnelling distance of $r = 4$ nm, $r' = 0.51$ and $\tau = 1$ s. Similarly for $r = 7.5$ nm, $r' = 0.96$ and $\tau = 1$ Ma. These values are indicated in figure 1 and are of the right order to account for our observations on tunnelling in feldspars (Huntley and Lamothe 2001, Huntley and Lian 2006).

Most of the data reviewed by Jonscher and de Polignac encompass a much shorter time scale, with some times as short as 1 ns, and the nature of the experiments is such that one can expect a much lower energy barrier. An example that may be more relevant to these data is: $E = 0.1$ eV, $\alpha = 1.6 \times 10^9 \text{ m}^{-1}$, $\rho' = 5 \times 10^{-5}$, $\rho = 5.1 \times 10^{16} \text{ cm}^{-3}$, $r = 18$ nm, $r' = 1.06$, and $\tau = 1$ ms.

The remarkable data of Cordier *et al* (1974), which cover nine orders of magnitude of time, have an exponent of -1.06 (see the replotted data in Jonscher and de Polignac 1984). For $\rho' = 2.4 \times 10^{-5}$, over the same range as shown for other values of ρ' in figure 3, the exponent is -1.06 . There is a very slight downwards curvature in the data of Cordier *et al*, as is also noticeable for the $\rho' = 5 \times 10^{-5}$ points in figure 3; arriving at any conclusion from this similarity is probably making too much of the theory.

The range of exponents found in figure 3 is -0.958 to -1.50 . Of the 24 exponents listed in the survey by Jonscher and de Polignac, table 1, all but six lie in this range; there are four values of 2 and two of 0.5. The values of 0.5 cannot be accounted for in the present theory, and may arise from two sets of traps (see Jonscher and de Polignac 1984, table 1). A value of 2 can be accounted for only over a limited time range by the present theory and this is in accord with the data summarized by Jonscher and de Polignac.

The theories of Thomas *et al* (1965), Riehl (1970), Delbecq *et al* (1974), Avouris and Morgan (1981) are in some ways more complex than the one presented here because of the situations that they attempt to describe. All of them omit the exponential term in equation (3), and hence miss the maximum in the $p(r)$ distribution which is responsible for the extended range of the power law.

It is easy to make predictions from the theory, though practical tests may not be easy. Varying the initial excitation pulse intensity will vary n_i , and the luminescence intensity should be proportional to it, but this is often likely to be the case in a theory. A more useful approach would be to vary the density of recombination centres. One should see the exponent starting at -0.95 and slowly becoming more negative as the concentration is increased. Also, the intensity should reach a maximum at $\rho' = [\ln(st)]^{-3}$; if this could be seen it would allow the determination of either s or α , assuming the other is known.

Thomas *et al* (1965) have suggested that equation (1) for the tunnelling probability should have an addition factor of r^m . While this will change the result in detail, it will not change the main features. Over a range of a factor of ~ 2 of r one can make a good approximation to r^m with $\exp(-cr)$, where c is a constant. Thus the effect is that of a modification to α .

The assumption that the recombination centres are randomly distributed may not always be valid. From the arguments advanced earlier it is apparent that there is a possibility of determining $p(r)$ from $I(t)$. Hama *et al* (1980) showed a nice method for doing this analytically using a Laplace transform; it does, however, require $I(t)$ data over many more orders of magnitude of time than is usually the case for it to provide a convincing distribution, and even then the assumption of the form of the tunnelling probability, equation (1), is a limitation.

Tunnelling may take place from the ground state of the trap; it may also take place from an excited state in which case population of the excited state can be either thermal or optical or

both. This situation has been considered by Avouris and Morgan (1981) in their explanation of luminescence decay of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphor. The above theory should be just as applicable, but with the frequency factor, s , multiplied by the fraction of time an electron spends in the excited state before it tunnels out. The constant α will be smaller than for the ground state. These factors will cause the probability of tunnelling from the excited state to be smaller or larger than that of tunnelling from the ground state.

4. Conclusion

A simple theory of tunnelling from electron traps to a random distribution of recombination centres is capable of explaining the power-law decay of luminescence that is observed with exponents ranging from -0.95 to -1.5 . Earlier tunnelling theories did not yield this result because they did not use the complete form of the distribution of tunnelling distances.

Acknowledgments

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada. R Visocekas and M J Aitken are thanked for inspiration.

References

- Aitken M J 1998 *An Introduction to Optical Dating* (Oxford: Oxford University Press)
- Avouris P and Morgan T N 1981 *J. Chem. Phys.* **74** 4347–55
- Bailiff I K and Barnett S M 1994 *Radiat. Meas.* **23** 541–5
- Bailiff I K and Poolton N R J 1991 *Radiat. Meas.* **18** 111–8
- Baril M R 2002 Spectral investigations of luminescence in feldspars *PhD Thesis* Simon Fraser University, Burnaby, BC, Canada
- Baril M R and Huntley D J 2003 *J. Phys.: Condens. Matter* **15** 8029–48
- Chen R and Kirsch Y 1981 *Analysis of Thermally Stimulated Processes* (Oxford: Pergamon)
- Chen R and Leung P L 2003 *Radiat. Meas.* **37** 519–26
- Cordier P, Delouis J-F, Kieffer F, Lapersonne C and Rigaut J 1974 *C.R. Acad. Sci., Paris C* **279** 589–91
- Delbecq C J, Toyozawa Y and Yuster P H 1974 *Phys. Rev. B* **9** 4497–505
- Gaunt P 1976 *Phil. Mag.* **34** 775
- Gaunt P 1986 *J. Appl. Phys.* **59** 4129
- Hama Y, Kimura Y, Tsumura M and Omi N 1980 *Chem. Phys.* **53** 115–22
- Huntley D J and Lamothe M 2001 *Can. J. Earth Sci.* **38** 1093–106
- Huntley D J and Lian O B 2006 *Q. Sci. Rev.* at press (accepted May 11, 2005 for the special issue honouring Professor J R Prescott's 80th birthday. A pdf file can be downloaded at: <http://www.sfu.ca/physics/research/workarea/huntley/publist.html>)
- Jonscher A K and de Polignac A 1984 *J. Phys. C: Solid State Phys.* **17** 6493–519
- Klik I and Chang C-R 1993 *Phys. Rev. B* **47** 9091–3
- McKeever S W S, Bøtter-Jensen L, Larsen N A and Duller G A T 1997 *Radiat. Meas.* **27** 161–70
- Randall J T and Wilkins M H F 1945 *Proc. R. Soc. A* **184** 390–407
- Riehl N 1970 *J. Lumin.* **1**, **2** 1–16
- Street R and Woolley J C 1949 *Proc. Phys. Soc. London A* **62** 562–72
- Street R, Woolley J C and Smith P B 1952 *Proc. Phys. Soc. London B* **65** 679–96
- Street R and Woolley J C 1956 *Proc. Phys. Soc. London B* **69** 1189–99
- Thomas D G, Hopfield J J and Augustyniak W M 1965 *Phys. Rev.* **140** A202–20
- Visocekas R 2002 *Radiat. Prot. Dosim.* **100** 45–54