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Limitations of conventional fitting methodology used for continuous wave optically stimulated luminescence (CWOSL) curves

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Abstract

Conventionally all CWOSL curves are fitted either as a single first order decaying exponential or sum of multiple first order decaying exponentials. This is the current practice followed and have been adopted by many investigators. This methodology is based on the assumption that all the traps participating in the OSL process obey only first order kinetics, which may not always be true. In this article, the limitations of conventional fitting methodology used for continuous wave optically stimulated luminescence (CWOSL) curves are comprehensively investigated using localized and delocalized models of luminescence for wide range of retrapping and recombination cross-section values. The study is also carried out using one trap one recombination centre (OTOR) as well as general order kinetics model of luminescence. In addition, the dependence of decay profile of CWOSL curves on radiation dose is also demonstrated. It is seen that a complex CWOSL curves may result from simple one trap one recombination centre model and the fitting of such curves as a sum of more than one first order decaying exponential may led to the misinterpretation of the OSL phenomena and there may be huge error in determination of photoionisation cross-section and order of kinetics. Examples are also demonstrated, where the CWOSL curve can be fitted as a sum of multiple first order decaying exponential despite the original CWOSL curve being a single non-first order curve and this must be taken into account, while carrying out kinetic analysis of CWOSL curves.

Keywords: *Continuous wave optically stimulated luminescence (CWOSL), Decaying exponential, Order of kinetics, Photoionisation cross-section.*

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1.0 Introduction

CWOSL curve is the variation of light output from a phosphor, when the stimulation is carried out optically. In this process, the stimulating intensity is constant during acquisition of the luminescence signal. During stimulation, the electrons are released from the traps and light is emitted if the recombination of electrons with holes is radiative. Further the released electrons may be retrapped (in the same trap), which may lead to slow luminescence decay. However in the absence of retrapping *i.e.* negligible retrapping; the luminescence decay is fast as compared to the case when retrapping is present. Futher the retrapping of the released electrons may take place in neighboring traps and the luminescence decay profile may differ from that expected from one trap one recombination centre model. The emitted luminescence can also arise, when electrons released from multiple traps recombine with holes and the resultant luminescence signal may be more complex. This also means that the luminescence arises due to recombination of electrons released from traps of varying activation energies *i.e.* more than one traps are contributing towards OSL. Sometimes linearly modulated OSL (LMOSL) may confirm number of traps participating and their individual contribution towards OSL. However this is true only when the values of photoionisation cross-section of the participating traps is not very close to each other for a given stimulation wavelength. Additionally the numbers of glow peaks during thermoluminescence (TL) recording also indicate the number of traps participating in the luminescence process and TL recording may sometime be advantageous as well resolved glow peaks are generally obtained. However all the TL peaks need/may not exhibit OSL, but all the OSL sensitive traps exhibit TL; although the thermal quenching effect if present may cause decrease in the luminescence (TL) efficiency. Another test which may indicate the optical sensitivity of the individual TL peaks or the traps participating in the process is to study the effect of optical bleaching at given wavelength on individual TL glow curves and if any optical bleaching/fading is observed, this only indicates the fact that a given TL peak may participate in the OSL process for a given optical wavelength. The point which needs to be mentioned is that the optical trap depth, $E^{`}$ (eV) is normally 2-3 times more than the thermal trap depth, E (eV). This happens because optical transitions follow selection rules and the gain of energy by the trapped electron during optical stimulation is one shot process whereas for thermal process, there is no such criteria and the required energy is gained in many collisions through phonons and is a multi shot process. Another question which requires attention is what decides that a particular trap will be optically sensitive/active or not? Why all TL traps are not optically active? The simple answer may be the value of photoionisation cross-section at a given stimulation wavelength; however comprehensive investigations about physics behind smaller or larger values of photo ionization cross-section are further needed.

As described earlier that the magnitude of retrapping coefficient/presence of retrapping during optical stimulation plays major role in deciding the shape of the curve. Also the information that the optically released electron moves to the excited state of the trap or to the conduction band, may be useful in the investigation of OSL process using an appropriate model. If the OSL curve is simultaneously accompanied with optically stimulated conductivity (OSC), then the recombination process occurs via conduction band. However if the OSL curve is not accompanied with OSC, then the recombination may occur via excited state of the trap. Normally the effect of retrapping on CWOSL curve shape is important when recombination takes place via conduction band because the electron released from the trap is free to move through the whole crystal where as for sub-conduction recombination, the traps and recombination centres are localized very near to each other and recombination and retrapping takes place within the same complex defect [1]. Further the presence of competing traps either leading to non-radiative recombination or presence of optically insensitive traps, may also affect the decay profile. The radiation dose, relative occupancy of traps and recombination centres and linear energy transfer (LET) variation/dependence may also complicate the nature of profile.

Some of the above mentioned points and their effect on OSL decay curves have been investigated by Chruscinska and co-workers [2-6]. In the series of papers, Chruscinska described the influence of trap coupling effect on shape of OSL decay. It was suggested that appearance of additional level can produce a deformation of OSL curve. A strong deformation, which makes impossible to deconvolute the OSL curve into first order components, informs about the incorrectness of the kinetic model assumption, but deformation, which does not lead to erroneous fitting procedure results, can be unrecognized [3]. Two cases of basic model (OTOR) widening *i.e.* additional TL trap and additional luminescence centre were considered by Chruscinska [3]. In addition, the influence of electron phonon interaction on the shape of OSL decay curve was also investigated [2, 4-6]. In this paper, the limitations of conventional fitting methodology used for continuous wave optically stimulated luminescence (CWOSL) curves are comprehensively investigated using localized and delocalized models of luminescence for wide range of retrapping and recombination cross-section values. The study is also carried out using general order kinetics (GOK) model of luminescence. In addition the dependence of decay profile of CWOSL curves on radiation dose is also demonstrated. It has been found that complex CWOSL curves may result by assuming simple one trap and one recombination centre model and the fitting of such curves as mixture of more than one first order decaying exponentials may led to misinterpretation of the OSL phenomena and can cause huge error in determination of photoionisation cross-section and order of kinetics. Examples are presented, where the CWOSL curve can be fitted as a sum of multiple first order decaying exponential however the original CWOSL curve may be a single CWOSL curve following non-first order kinetics. It is demonstrated that conventional fitting with one or more first order decaying exponential components may not be appropriate and such situations are easily encountered while investigating OTOR and GOK models.

2. The models

a. One trap one recombination centre model:

The energy level scheme shown in Fig. 1 is a simple one trap one recombination centre (OTOR) model. One trapping state with activation energy E having concentration of N (m^{-3}) capable of trapping electrons is assumed to be active. The optical stimulation of a pre-exposed sample raises electrons to the conduction band, out of which some are re-trapped and others may recombine, there by producing OSL photons. If σ_p is excitation cross-section (photo-ionization cross-section) of the trap for stimulating radiation having intensity I and frequency ν (wavelength, λ), then n * ($\sigma_p I/h\nu$) is the rate at which the stimulating light release electrons from the filled traps n (m^{-3}). In view of above, the equations governing the OSL process are [7]

$$\frac{dm}{dt} = -\sigma_m v m n_c = -A_m m n_c \tag{1.1}$$

$$\frac{dn}{dt} = -\frac{\sigma_p I n}{h\nu} + \sigma_T v (N-n) n_c = -\frac{\sigma_p I n}{h\nu} + A_n (N-n) n_c \tag{12}$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} = \frac{\sigma_p I n}{h\nu} - n_c [A_n (N-n) + A_m m] \tag{1.3}$$

where

n_c is instantaneous concentration of electrons in conduction band (m^{-3}), m, n are instantaneous concentration of recombination centres and electron traps (m^{-3}), N is total concentration of electron traps (m^{-3}), A_m (σ_m v) and A_n (σ_T v) are recombination and re-trapping coefficients (m^3 s^{-1}), σ_T and σ_m are retrapping and recombination cross-sections (m^2) of the trap and recombination centre respectively, v is velocity of conduction electrons (m s^{-1}), h, the Planck's constant ($6.62*10^{-34}$ J s), ν is frequency of stimulating radiation (Hz), I is intensity of stimulating radiation ($Jm^{-2}s^{-1}$) and σ_P is excitation/photoionization cross-section of a given trap for stimulating radiation. It should be noted that photoionization cross-section, σ_P of the trap is different from the retrapping cross-sections, σ_T (even σ_m). Physically σ_T represents cross-section to capture the mobile electrons whereas σ_P represents how stimulating light interact with the electron trapped in the potential well, so that it can be released optically. The value of σ_P decides, whether the trap will be optically active or not.

In the set of equations (1.1-1.3), ($\sigma_P I/h\nu$) has the dimensions of s^{-1} and represents optical excitation rate, f (s^{-1}). If I is assumed to be of order of few $mWcm^{-2}$, $h\nu$ of order of few eV and σ_P having variation from 10^{-20}-10^{-25} m^2, then ($\sigma_P I/h\nu$) = f may vary from 10-10^{-5} s^{-1}. The value of f is constant for while recording CWOSL curves. Using $f = (\sigma_P I/h\nu)$, A_m (=σ_mv) and A_n (=σ_T v) in the set of equations (1.1-1.3), we have

$$\frac{dm}{dt} = -A_m m n_c \qquad (1.1a)$$

$$\frac{dn}{dt} = -nf + A_n(N-n)n_c \qquad (1.2a)$$

$$\frac{dn_c}{dt} = nf - n_c[A_n(N-n) + A_m m] \qquad (1.3a)$$

The intensity of OSL signal I, is proportional to the rate of recombination and is given by

$$I = -\frac{dm}{dt} = A_m m n_c \qquad (1.4)$$

The set of equations can further be simplified by assuming the quasi-equilibrium (QE) condition, *i.e.* $n_c << n$ and $\frac{dn_c}{dt} << \frac{dn}{dt}$; i.e. $dm/dt \cong dn/dt$. By putting $\frac{dn_c}{dt} = 0$, in the set of equations (1.1a-1.3a), we have

$$n_c = fn/(A_n(N-n) + A_m m) \qquad (1.5)$$

Using the value of n_c from equation (1.5) in equation (1.4), we have

$$I = \frac{A_m mnf}{[A_n(N-n) + A_m m]} \qquad (1.6)$$

The limiting cases of the equation (1.6) are

(1) If $A_n = 0$, *i. e.* no re-trapping, then $I = nf$ and always represent first order kinetics.

(2) If $A_n(N-n) >> A_m m$, *i. e.* strong re-trapping, then $I = \frac{A_m mnf}{A_n(N-n)}$. Which for $m = n$ reduces to $I = \frac{A_m n^2 f}{A_n(N-n)}$ and further for $N >> n$ (with $m = n$), we have $I = \frac{A_m n^2 f}{A_n N}$ and represents OSL curves which are governed by second order kinetics for $A_n = A_m$.

(3) If $A_n = A_m$, then $I = \frac{mnf}{(N-n+m)}$, which for $m = n$ reduces to $I = \frac{n^2 f}{N}$ and represents second order kinetics.

b. General order kinetics model

On the basis of general order kinetics (GOK), the OSL intensity I can be written as [7-9]

$$I = -\frac{dn}{dt} = f\frac{n^b}{N^{b-1}} \qquad \textbf{(1.7)}$$

where b is the order of kinetics and the meaning of other parameters is same as described earlier. Further the equation (1.7) reduces to first order equation:

If $b = 1$, we have first order kinetics represented by the following equation

$$I = -\frac{dn}{dt} = nf \qquad (1.7a)$$

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Further if $b = 2$, we have

$$I = -\frac{dn}{dt} = f\,\frac{n^2}{N} \qquad (1.7b)$$

which represents second order kinetics.

c. Model based on localised transitions

Localized transitions represent sub-conduction recombination process in which the electrons released from the traps during optical stimulation are not raised to the conduction band, but to an energy state below conduction band and further from the excited state of the trap, the electrons can be retrapped to the ground state of the same trap or recombine with the holes/recombination centres which are in its immediate vicinity. In the simplest form, the intensity of luminescence for process in localized recombination model is

$$I = -\frac{dn}{dt} = n\,f \qquad (1.8)$$

Based upon the above equation, the CWOSL curve always follow first order kinetics whether the reaction is retrapping dominant or recombination dominant because the traps and recombination centres are within a single complex defect and the trapping and the recombination transitions take place within a single defect complex. It should be noted that CWOSL curves arising from localized recombination always exhibit first order kinetics and are best fitted using first order decaying exponential. Also the CWOSL curve is not accompanied with OSC.

The above equations have been used in the present study to investigate the OSL phenomena. The curves are simulated for wide range of retrapping, recombination coefficients, radiation doses and kinetic orders. Further the limitations of conventional fitting methodology used continuous wave optically stimulated luminescence (CWOSL) curves are comprehensively investigated.

A CW OSL curve follows first order kinetics if it is fitted by single decaying exponential and the decay constant/pattern is always independent of radiation dose and is unaffected by optical bleaching. For all these experimental conditions, the plot of $\ln(I_{CW})$ versus time is a straight line, where I_{CW} is CWOSL intensity. It is also worth mentioning that for non-first order kinetics, the decay pattern for CWOSL curve is not a perfect decaying exponential and the decay constant/pattern is dose as well as order of kinetics dependent. The decay constant for CWOSL curves is influenced by optical bleaching. With repeated bleaching, few components may be bleached.

3. Numerical study

The set of equations (1.1a-1.3a/1.7) are solved for constant wave stimulation profile (f = constant) under various conditions: i) There is no re-trapping i. e. $A_n = 0$ or $A_m >> A_n$, ii) Re-trapping is relatively strong i. e. $A_n(N-n) >> m\ A_m$ and iii) Re-trapping and recombination coefficients are equal *i. e.* $A_m = A_n$. The values of parameters used in the simulation are $f = 10^{-2}\ s^{-1}$, $N = 10^{23}\ m^{-3}$ and A_m and A_n are assumed to be in the range $10^{-14} - 10^{-22}\ m^3\ s^{-1}$. Various combinations of A_m and A_n are tried. In Fig. 2a, the CWOSL curves for various radiation doses are shown whereas in Fig. 2b, the effect of the value of retrapping coefficient on the shape of CWOSL curve are shown. Similarly for GOK, the CWOSL curves for various kinetic order values are shown and it is seen that with the increase in the value of order of kinetics, the decay of OSL curves becomes slow implying that more time is required to acquire the complete signal. Further in Figs. 3a and 3b, CWOSL curves for various b values and doses in GOK model are shown. Since the CWOSL curves resulting from localized recombination are perfect decaying exponential and always represent first order kinetics whether retrapping is present or absent, so the simulated curves are not shown. These CWOSL curves are best fitted by first order decaying exponential and the kinetics analysis based on fitting always represent the actual parameters.

4. Analysis using conventional first order decaying exponentials fits

The CWOSL curves studied using OTOR and GOK model are analyzed using conventional fit obeying decaying exponential as decomposition of CWOSL curve into 1 or 2 or 3 or more components is a common practice [3]. For first order decay exponential we have, A_1*exp($-ft$) where A_1 is a constant reflecting percentage of the component present and f is decay constant and t is time. Similarly decaying exponential fits of second and third order is also possible. As described earlier, the decay constant f is ($\sigma_p I/h\nu$), so the value of photoionisation cross-section (σ_p) of the trap can be determined as other parameters such as I and $h\nu$ are known experimentally. In this paper, the value of the decay constant f as a result of particular fit is also compared with the actual value of f previously assumed during simulation. The results are shown in Tables 1-4.

5. Results and discussion

The OSL curves obtained for constant wave stimulation are shown in Fig. 2a and 2b respectively for $f = 10^{-2}$ s^{-1}. From Fig. 2a, it is seen that with the decrease in radiation dose, the fall/decay of the OSL curves is slow, implying that more time is required to acquire the complete signal. From Fig. 2a, it is also seen that for a given a CW stimulation profile and same acquisition time - less OSL signal is erased for the sample exposed to low dose whereas for the sample exposed to high dose, more OSL signal is erased. Similar results have been found for $f = 10^{-1}$ s^{-1}. In addition to above, same study has been carried out for various values of the retrapping coefficients (A_n) *i.e.* in the range 10^{-23}-10^{-16} m^3 s^{-1} and results are shown in Fig. 2b. It has been found that with increase in the value of A_n, the fall/decay of curves is fast initially after which it becomes flat, however further acquisition of the curve shows that the OSL signal, which is left for recording via second or higher readouts is more for higher retrapping coefficients, implying that the curves with higher retrapping coefficients appear with slowly falling tail whose magnitude increases with the increase in the value of retrapping coefficient.

In Table -1, the results pertaining to Fig. 2a are analyzed. It has been found that for a given set of parameters, the decay constant is dose dependent. The estimated value of f from first order fits differs from that assumed theoretically except at high doses, which implies that there will be huge errors while estimating the value of photoionisation cross-section (σ_p). This only implies that sometimes the conventional fitting of CWOSL curves using decaying exponential of first or higher order may lead to misinterpretation of the luminescence kinetics. It is also found that the value of the decay constant decreases as the doses decreases. Similar results are shown for Fig. 2b in Table-2 and it has been found that for first order kinetics, the first order decaying exponential fit provides the exact values of σ_p, whereas in other cases it is possible to fit multiple exponentials, but that may not be the actual situation. Similarly in Table-3 and 4, the results of fitting for Figs. 3a and 3b are shown. It has been found that for the values of f or σ_p obtained using second or third order decaying exponential fits may not be the actual values for CWOSL curves resulting from traps obeying non-first order kinetics. Similar results are shown in Table-4 at various doses for $b = 1.6$. The study also shows that for $b = 2$, the CWOSL curve can be fitted as sum of two or three decaying exponentials and this will lead to wrong interpretation of the CWOSL curves because it is already known that the above curve obeys second order kinetics. Many examples of this type are possible and the interpretation of CWOSL curves obeying non-first order kinetics into sum of slow, medium or fast components (exponentials having different decay constant) is wrong/erroneous. Chruscinska [2-6] has also observed deviations from first order kinetics, while investigating OSL by considering presence of competing traps in OTOR model.

Hence complex CWOSL curves may result from simple one trap and one recombination centre model and the fitting of such curves as a sum of more than one first order decaying exponential (as demonstrated) may lead to the misinterpretation of the OSL phenomena; there may be huge error in determination of photoionisation cross-section and order of kinetics. Many examples are demonstrated, where the CWOSL curve can be fitted as a sum of multiple first order decaying exponential; however the original CWOSL curve may be a single non-exponential component rather than composed of multiple components and this must be taken into account, while carrying out kinetic analysis of CWOSL curves.

6. Conclusions

It has been found that:

i. CWOSL curves obeying first order kinetics (delocalized recombination model) *i.e.* negligible retrapping during optical stimulation are best fitted using decaying exponential of first order and the value of the decay constant, f or photoionisation cross-section σ_p are obtained from the fit are the actual values.

ii. The CWOSL curves resulting from localized recombination are perfect decaying exponential and always represent first order kinetics, whether retrapping is present or absent. These curves are best fitted by first order decaying exponential and the kinetics analysis based on fitting always provide actual parameters of the trap.

iii. There could be huge error in the determination of the value of decay constant, f or photoionisation cross-section σ_p if fits using decaying exponential are used to approximate CWOSL curves actually obeying non-first order kinetics *i.e.* a CWOSL curve obeying second order kinetics may be fitted as sum of slow, medium and fast components although it is actually a non-first order curve. Hence the conventional fitting with one or more first order decaying exponential components may not always be appropriate in many cases.

iv. Preferably it is better to perform other tests such as optical bleaching, TL and LM OSL studies, dose dependence *etc.* for having more information pertaining to traps and recombination centres participating in the luminescence process.

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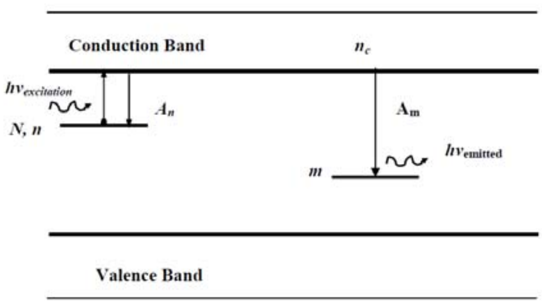

Fig. 1: One trap one recombination centre model (OTOR) model. The designations are given in the text.

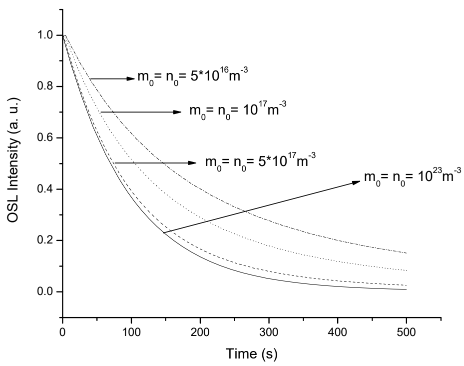

Fig. 2a: Dose dependence for curves in OTOR model. The other parameters assumed theoretically are $A_m = 10^{-17}$ m^{3}s^{-1}, $A_n = 10^{-23}$ m^{3}s^{-1}, $f = 10^{-2}$ s^{-1} and $N = 10^{23}$ m^{-3}.

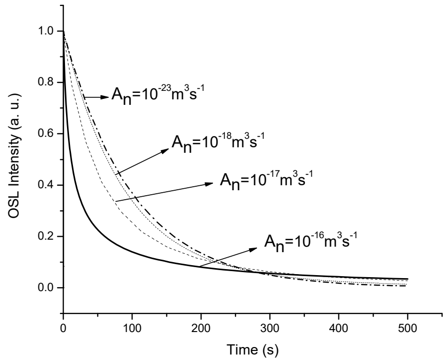

Fig. 2b: Dependence of curves on A_n in OTOR model. The other parameters assumed theoretically are $A_m = 10^{-17}$ m^{3}s^{-1}, $f = 10^{-2}$ s^{-1} and $N = 10^{23}$ m^{-3}.

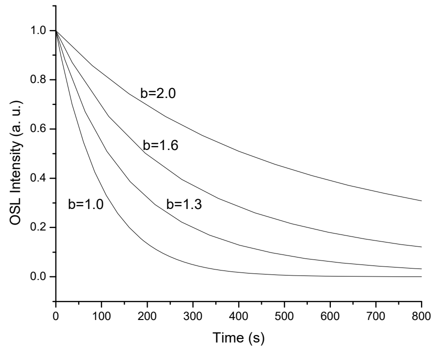

Fig. 3a: CWOSL curves for various b values in GOK model. The other parameters are $f = 10^{-2}$ s^{-1}, $n_0 = 10^{22}$m^{-3} and $N = 10^{23}$ m^{-3}.

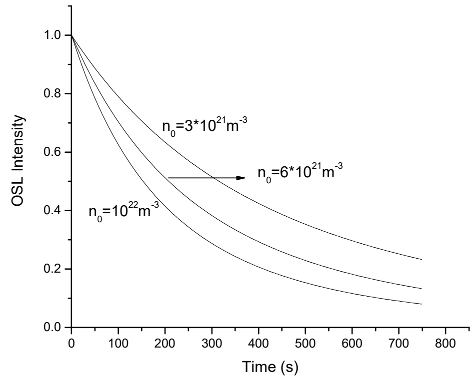

Fig. 3b: Dose dependence of CWOSL curves for $b = 1.6$ in GOK model. The other parameters assumed theoretically are $f = 10^{-2}$ s^{-1} & $N = 10^{23}$ m^{-3}. For $b = 1$, the curves are independent of dose. Similar results are obtained for other values of b, except $b = 1$.

Table – 1: Dose dependence of CWOSL curves. The other parameters assumed theoretically are A_m =10^{-17} m^3s^{-1}, A_n =10^{-23} m^3s^{-1}, f= 10^{-2} s^{-1} and N =10^{23} m^{-3}.

Dose; n_0 (m^{-3})	**Number of components of exponential decay**	χ^2	f^* (s^{-1}) ($f_{assumed}$ = 10^{-2} s^{-1})
10^{23}	1; first order	1	0.01
5 * 10^{17}	1; first order	0.99993	0.0098
10^{17}	1; first order	0.9997	0.0075
5 * 10^{16}	1; first order	0.99979	0.00574
	2; second order	1	0.0033 0.0090

Table – 2: Dependence of curve shape on A_n. The other parameters assumed theoretically are A_m =10^{-17} m^3s^{-1}, f= 10^{-2} s^{-1} and m_0= n_0= 10^{23} m^{-3}.

Retrapping coefficient; A_n (m^3s^{-1})	**Number of components of exponential decay**	χ^2	f^* (s^{-1}) ($f_{assumed}$ = 10^{-2} s^{-1})
10^{-23}	1; first order	1	0.01
10^{-18}	1; first order	0.99998	0.011
10^{-17}	1; first order	0.9984	0.017
	2; second order	0.99999	0.0083 0.030
10^{-16}	1; first order	0.97755	0.0507
	2; second order	0.99919	0.0161 0.15
	3; third order	0.99997	0.0086 0.0546 0.262

Table - 3: Analysis of CWOSL curves for various values of order of kinetics, b. The other parameters assumed theoretically are f = 10^{-2} s^{-1}, n_0 = 10^{22} m^{-3} and N =10^{23} m^{-3}.

Order of kinetics; b	**Number of components of exponential decay**	χ^2	f^* (s^{-1}) ($f_{assumed}$ = 10^{-2} s^{-1})
1.0	1; first order	1	0.01
1.3	1; first order	0.999	0.0061
	2; second order	1	0.0097 0.0040
1.6	1; first order	0.999	0.0040
	2; second order	1	0.0025 0.0072
2.0	1; first order	0.999	0.0023
	2; second order	1	0.0039 0.0012
	3; third order	1	0.0015 0.0045 0.0015

Table – 4: Dose dependence of curves for b = 1.6 in GOK model. The other parameters assumed theoretically are f= 10^{-2} s^{-1} and N =10^{23} m^{-3}. Similar results are obtained for other values of b, except b = 1. For b = 1.0, the curves are independent of dose and obey first order decay exponential.

Dose; n_0 (m^{-3})	**Number of components of exponential decay**	χ^2	f^* (s^{-1}) ($f_{assumed}$ = 10^{-2} s^{-1})
10^{22}	1; first order	0.99952	0.0040
	2; second order	1	0.0025 0.0072
3 * 10^{22}	1; first order	0.99975	0.0037
	2; second order	1	0.0064 0.0025
6 * 10^{22}	1; first order	0.99993	0.0026
	2; second order	1	0.0017 0.0044