Stepwise Deconvolution of Thermoluminescence Glow Curve

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Abstract

Thermoluminescence (TL) is a property of some materials utilized to measure the radiation dose in a material exposed to a radiation source for a period of time. Dosimeter is based in the measure of the light that a material emit when it is heated after radiation. The TL response in a material can be derived by the band gap theory of solids. In this work, glow curves are modeled following a deconvolution process using Gaussian curves sequentially. One by one, Gaussian curves are added, and every time one is added, manual fitting is carried to provide an initial solution followed by computer optimization. The process repeats until their contribution of new Gaussian curves in reducing the fitting errors is no longer significant and the behavior of errors is considered stable. To illustrate the methodology, glow curves from diamond like carbon are analyzed. The deconvolution method is carried and explained step by step until an acceptable fit is found. In addition, a relatively simple linear prediction approach to perform interpolation is proposed and discussed. Physical implications of the modeled phenomena of electrons traps are discussed for each deconvolution peak and the corresponding energy levels are measured.

Keywords: Thermoluminescence, Deconvolution, Diamond Like Carbon.

Recibido , Aceptado

I. Introduction

Thermoluminescence (TL), a phenomenon that some materials exhibit, is the emission of light when a material is heated after it was irradiated. Dosimeter is an instrument that measures the radiation dose in a material exposed to a radiation source for a period of time. Dosimeter is based on the measurement of light intensity that a material emits when it is heated [1–3]. TL response in a material can be derived by the band gap theory of solids, in an ideal semiconductor or electrical insulator crystal, electrons lies preferable in the valence band, the next energetic band that can be occupied by the electrons is the conduction band, both bands are separated by the very known band gap, diamond has a band gap up to 5.4 ev.

Radiant absorption energy bigger than Fermi equilibrium line will produce the electron valence ionization generating holes in the valence band and free electrons in the conduction band [4]. In an electrical insulator and semiconductor materials, certain percentage of free charges lies trapping between both bands, these free charges and trapping electrons have different energy distribution, some models for this have been proposed [5].

Diamond films synthesized from Chemical Vapor Deposition (CVD) techniques, have been reported as an excellent prospect for thermo luminescence dosimeter involving ionizing and non ionizing radiation fields [6–7].

The CVD diamond TL properties depend on the physical chemical conditions of the precursor gas, and there are unresolved problems for the reproducibility and the homogeneity of the samples that must be solved.

Despite the progress of CVD diamond growth from gas mixtures, scarce work concerning the synthesis of diamond using liquid organic compounds as precursors by the pulsed liquid injection chemical vapor deposition technique assuring good

reproducibility of samples synthesis has been used as TL dosimeter [8–9].

In this work, a simple deconvolution method is presented and applied to model observations form light intensity data of a dosimeter curve obtained directly from the glow curve [10]. As a result, a model with an acceptable fit was found, energy levels of electrons traps are calculated, and prediction capability through linear interpolation is discussed.

II. Deconvolution procedure

In functional analysis, a convolution is an operation between two functions to create a third one by generalizing the concept of moving average. However, in physics, a convolution process can be understood as an application of the superposition principle, where the net response at a given place and time is caused by the sum of other individual stimuli. This way, in this research, a deconvolution process is defined as a mathematical method used to identify elementary functions whose sum creates a new and more complex function that represents the behavior of the observations under analysis.

Glow curves in TL represent complex functions, and a Deconvolution process can be used to find simple functions that represent different traps of energy (glow peaks) whose sum gives the glow curve under analysis. One approach to model glow curves consist in using existing probabilistic distributions functions as elementary functions. However, probability functions cannot be used as they are. Normalizing constants have to be taken out; otherwise the area under the curves will always be 1. This way, only the kernel of a probability distribution is used to fit the data. For instance, the kernel of a normal function (Gaussian function) is used as follows:

$$g_{di}(T|\mu_{di},\sigma_{di},H_{di}) = H_{di}\exp\left[\frac{1}{2}\left(\frac{T-\mu_{di}}{\sigma_{di}}\right)^2\right], i=1,2,\ldots,n;\ d\in\Re \qquad (1)$$

where T is the temperature, μ_{di} controls the location of the maximum of the function, σ_{di} controls the scale, and H_{di} is added to control the high at different dose (d) levels.
Where i is used as an index that runs from 1 to *n* to enumerate the number of functions that are convoluted together. Finally, n represents the number of elementary functions within the convolution. (Eq 1) can be used to create a superposition of functions to model the behavior of the TL intensity I_d at different dose levels.

$$\hat{I}_d = c_d + \sum_{i=1}^{n} g_{di}\left(T|\mu_{di},\sigma_{di},H_{di}\right) \qquad (2)$$

where c_d stands for a constant used to fit the data at dose level d. $\hat{I}_d$ represent the TL intensity estimated by the model.

The process of Deconvolution consists on finding the value of the constant, the right amount n elementary functions, and their corresponding parameter values that together creates a superposition of functions that gives shape to the TL glow curve represented by the collected data. To find the parameter values that give the best fit, many loss functions can be used to be minimized. One "common" lost function in nonlinear modeling is the quadratic loss function. The minimization of this function gives least squared estimates of parameters. As long as no outliers are found in the data, a quadratic loss function should be capable of giving parameter values that best fit the available observations. The loss function used in this research was:

$$O = \sum_{j=1}^{k}\left(I_{dj} - \hat{I}_{dj}\right)^2 \qquad (3)$$

Here, the index j represents the individual observations obtained at different d levels. Since $\hat{I}_{dj}$ stands for the estimated intensity (fitted model), from (Eq. 2), and I_{dj} stands for the observed value, the parameter values obtained are the ones that minimize the cumulated square error between the model and the data.

III. Thermoluminiscense modeling of Carbon like diamond

The modeling process follows five major phases, (1) data gathering, (2) curve fitting, (3) verification, (4) interpolation analysis, and (5) model interpretation. Overall, the data gathering process was done through the reconstruction of experimental results stored in a computer image. Image pixels were studied to get the coordinates of the plotted data. Curve fitting was done via curve deconvolution. In total, five Gaussian curves were added together to fit the data at every dose level studied, from 100 Gray (Gy) to 1600.

Verification was carried by showing that errors around each curve are homocedastic, stationary, and independent enough to conclude that a good fit was found. Additionally, to make results practical, TL intensity can be predicted at any dose level within the range studied by following a linear interpolation. Finally, it is hypothesized that each Gaussian curve represents individual energy traps that are released as temperature increases for each dose level.

III–I Data gathering

Original data was not available, only an image from the data remained as seen in Fig. 1. To recover the loss information, a "forensic" analysis of this image was carried out. This analysis involved the recovery of pixels coordinates of each data point within the figure rescaled to fit the measures of each axis.

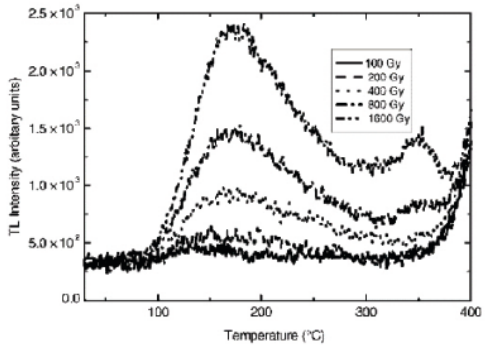

Fig. 1. Image describing original experiments (from Morales et al. [10])

It is evident that errors occur during the recovery process. However, the major concern is not within the individual values, but the average trend of the data, which is more robust to small departures of the individuals. Fig. 2 shows the result of this recovery process, an image where each point can be overlapped almost perfectly over the original ones. Variation between original observations and extracted coordinates is smaller than variation within neighboring observations. Hence, it seems reasonable to believe that the extraction process provides precise enough observations for a curve fitting to be carried away.

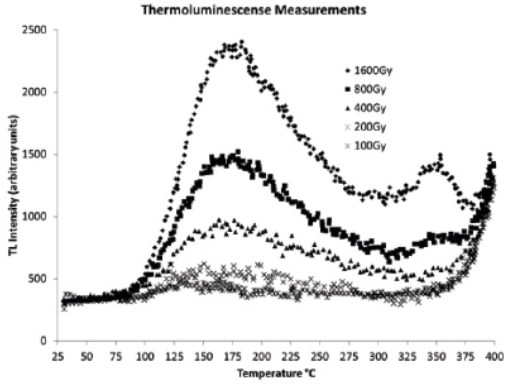

Fig. 2. Recovered measurements from a "forensic" data analysis.

The modeling process makes use of the recovered data to fit convoluted Gaussian curves capable of emulating a large number of shapes within the range of the data under analysis.

III–II Curve Fitting and Verification

Fitting a superposition of several curves with many parameters might lead to optimization problems due to the existence of local optimal points. To avoid this issue it is advisable to use graphical programs with some understanding of the properties of the parameters within each function. This way, a manual calibration can be performed followed by a computerized search for parameter values that minimize the loss function. A multi-starting search procedure is desirable to have when doing the fitting.
Also, as a principle, it seems reasonable to think that the model should be as simple as possible.

This reduces the risk of over parameterization, and increases the possibilities for interpretation. Following the routine described in Fig. 3, the modeling starts by fitting (Eq. 2) with only one normal kernel until the residuals within the model, defined in (Eq. 4), show a homoscedastic behavior over the temperature t_j and fitted values $\hat{I}_{dj}$ with no signs of a trend that might suggest dependency between errors, and scattered around zero with no outlying observations. A scatter plot between variables is enough to assess residuals in most cases, however, some experience observing residuals might be required.

$$e_{dj} = I_{dj} - \hat{I}_{dj} \tag{4}$$

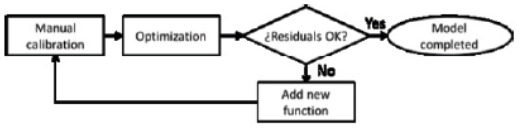

Fig. 3. Curve fitting and verification process

Manual calibration is addressed by adding one term from (Eq. 2) at a time followed by a residual inspection. When no terms have been added to the model, it can be said that the residuals are the observations themselves. To initialize the constant, the overall minimum observed TL intensity can be used. Then, the constant is subtracted from the data to get a new set of residuals. After that, a new term is added, which is a Gaussian function as described in (Eq. 1). To initialize the Gaussian function it is necessary to find a peak within the new observed residual data (if no peak is found within the range of the residuals, it can be mentally extrapolated), the temperature at the peak selected defines μ_{di}, and the TL intensity at the peak defines H_{di}. To initialize σ_{di}, it is necessary to keep in mind that the Gaussian function is a bell shaped function, where each inflexion point is located at $T = \mu_{di} \pm \sigma_{di}$ with an intensity of $H_{di} e^{-\frac{1}{2}} \approx 0.6 H_{di}$. In other words, the initial values of σ_{di} can be obtained by the estimated half width of the bell shape at 60% of the peak altitude. Table 1 shows the initialization values manually obtained for a dose of 1600 Gy using five Gaussian functions. Plots of the curves being fitted and the residuals over the temperature greatly help with the visualization process. It can be seen in Fig. 4 that the initial parameters values offer a marginal fit to the data, mostly after temperatures of 200 °C where the original data shows a more complex form. Fitting issues are highlighted in the residuals plot presented in Fig. 5.

Overall the residuals do not look homoscedastic and trends are showing, clear signs of a lack of fit. Nevertheless, this is only a manual fitting with initialization parameters that serves as input for a computerized optimization.

Using GRC Nonlinear procedure with Excel solver, and a convergence criterion of 0.0001, parameter values are optimized by minimizing the sum of squared errors. The new parameter values are the least squared estimators of the data. Fitted model and model errors are shown in Fig. 6 and Fig. 7. Least squared estimates for each curve are summarized in Fig. 8, and the corresponding parameters of each function are seen in Table 2. Finally, the process is repeated for each glow curve until all observations within the experiment are modeled.

Table 1. Initialization values for a dose of 1600 Gy

i	H_{1600i}	$\propto_{di}$	σ_{1600i}
1	1,984.000	170.000	35.000
2	1,100.000	240.000	33.000
3	737.000	305.000	31.000
4	975.000	350.000	27.000
5	1,015.000	400.000	11.000
c_{1600}	308.300		

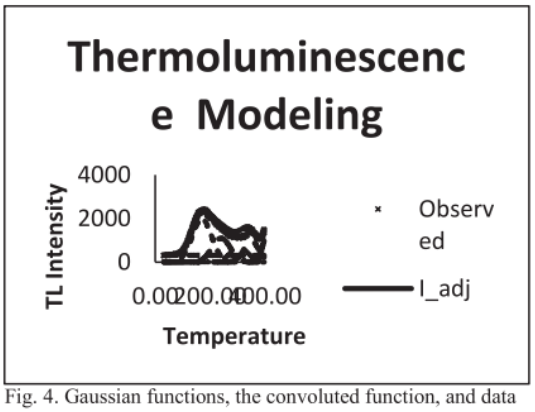

Fig. 4. Gaussian functions, the convoluted function, and data using initialization parameters

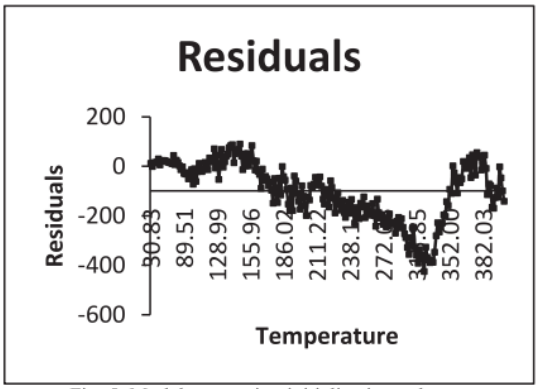

Fig. 5. Model error using initialization values

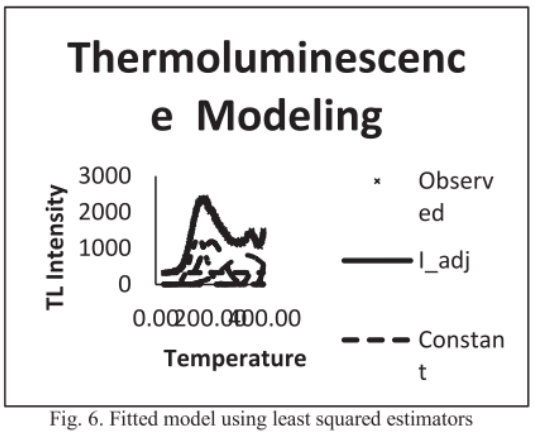

Fig. 6. Fitted model using least squared estimators

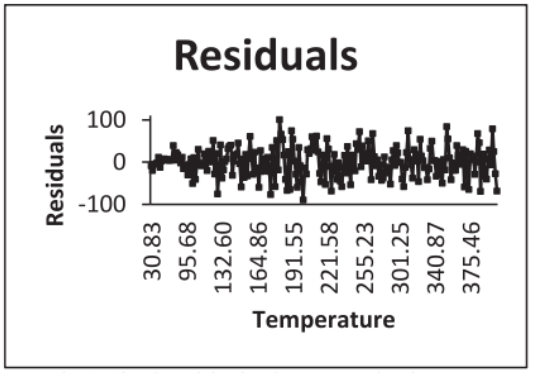

Fig. 7. Fitted model using least squared estimators

Table 2. Estimated parameters from the deconvolution process of carbon like diamonds.

Dose (d)	Parameter	Gaussian Curve (i) 1	2	3	4	5	c_d
1600 Gy	H_{1600i}	1263.435	1183.092	808.546	306.663	1965.757	327.932
	$\propto_{1600i}$	157.387	206.507	332.292	351.176	423.333	
	σ_{1600i}	28.967	41.347	75.973	13.551	16.655	
800 Gy	H_{800i}	501.774	700.828	474.667	310.675	2311.311	319.797
	$\propto_{800i}$	147.870	186.465	262.945	351.962	439.435	
	σ_{800i}	27.727	37.874	59.308	19.326	31.735	
400 Gy	H_{400i}	358.985	345.956	1661.321	363.676	n.a.	331.110
	$\propto_{400i}$	154.771	215.006	433.373	540.350	n.a.	
	σ_{400i}	32.955	54.449	27.080	167.373	n.a.	
200 Gy	H_{200i}	127.140	217.085	1140.864	110.203	n.a.	303.931
	$\propto_{200i}$	140.631	201.418	411.236	359.591	n.a.	
	σ_{200i}	22.466	59.899	18.635	16.259	n.a.	
100 Gy	H_{100i}	101.481	36.699	1598.074	413.531	n.a.	344.093
	$\propto_{100i}$	144.330	231.627	428.348	536.651	n.a.	
	σ_{100i}	26.453	53.032	25.056	92.101	n.a.	

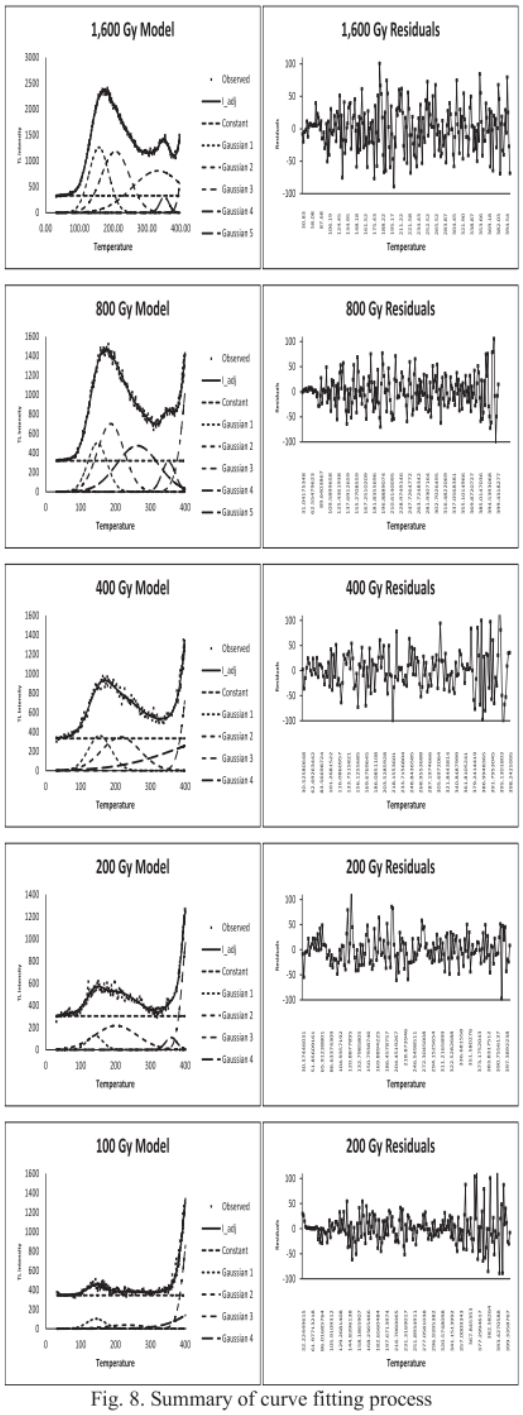

Fig. 8. Summary of curve fitting process

As seen in Fig. 8, glow curve from a dose of 100 to 400 were fitted using four Gaussian functions, whereas the rest (800 and 1,600 Gy) needed five. Residuals in every curve look stationary with no evident trend, which means they are fairly independent, giving indication of a good fit. Only residuals from a dose of 100 present an increment in their dispersion, while the rest look homocedastic. The increment in variation at high temperature can be expected when realizing that TL intensity at highest temperatures raise with a larger slope than the rest small in temperature measurements provoke large variation in TL intensity.

III-III Model interpolation

To make the model practical, it is convenient to have an adequate interpolation method. One simple form of interpolation is linear interpolation, where a desired intensity $\hat{I}_{dt}$ is predicted by using the predicted intensity values obtained at temperature T at the immediately higher and immediately lower doses found in Fig. 2, called d_{high} and d_{low} respectively. The corresponding TL intensities for those dose values are $\hat{I}_{high,T}$ and $\hat{I}_{low,T}$ where the sub-index indicates the matching dose (high or low). This way, linear interpolation can be performed using (Eq. 5).

$$\hat{I}_{dT} = \frac{(d_{high} - d)\hat{I}_{high,T} + (d - d_{low})\hat{I}_{low,T}}{d_{high} - d_{low}} \qquad (5)$$

For instance, if a TL intensity need to be estimated for a dose of 1,000 Gy and a temperature of 300 °C, defined as $\hat{I}_{1000,300}$, then it is necessary to make use of intensity values calculated using the parameters shown in Fig. 2 for $\hat{I}_{high,300} = \hat{I}_{1600,300} = 1158.68$ and $\hat{I}_{low,300} = \hat{I}_{800,300} = 726.65$. This lead to the following interpolation:

$$\hat{I}_{dT} = \frac{(1{,}600 - 1{,}000)1{,}158.58 + (1{,}000 - 800)726.65}{1{,}600 - 800} = 1050.598 \qquad (6)$$

Additionally, by using all fitted glow curves from Fig. 2 it is possible to regress a second or third degree polynomial at the desired temperature in order to have a better interpolation. However, to assume a specific curvature between glow curves with only five observations seems too risky, but it is up to the analyst to decide. Finally, it is tempting to regress the parameters presented in Table 2 with the different dose levels in an attempt to unify all glow curves.

However, if one is up to that, individual fitting of glow curves is lost, and no knowledge about possible gains in interpolation precision exists.

Hence, this approach should be avoided unless data between existing glow curves is obtained. Data between dose levels is required to find the best interpolation method.

III-IV Model interpretation by energy measurements

The trap energy of the electrons were calculated with the formula reported by Kitis et al, [11]. The values for the trap are presented in the Table 3.

Table 3. Values trap energy and deconvolution parameters for doses up to 1600 Gy.

Dose, Gy	μ	σ, K	T_{Max} K	T1, K	T2, K	E, eV
100	144.330	26.453	417.480	370.550	464.410	0.560
	231.627	53.032	504.777	410.693	598.861	0.408
	428.348	25.056	701.498	657.046	745.950	1.669
	536.651	92.101	809.801	646.405	973.197	0.605
200	140.631	22.466	413.781	373.924	453.638	0.648
	147.418	59.899	474.568	368.301	580.835	0.320
	411.236	18.635	684.386	651.326	717.446	2.137
	359.591	16.259	632.741	603.896	661.586	2.093
400	154.771	32.955	427.921	369.456	486.386	0.472
	215.006	54.449	488.156	391.558	584.754	0.372
	433.373	27.080	706.523	658.480	754.566	1.567
	540.350	167.373	813.500	516.564	1110.436	0.336
800	147.870	27.727	421.020	371.830	470.210	0.543
	186.465	37.874	459.615	392.423	526.807	0.474
	262.945	59.308	536.095	430.877	641.313	0.412
	351.962	19.326	625.112	590.826	659.398	1.719
	439.435	31.735	712.585	656.284	768.886	1.360
1600	157.387	28.967	430.537	379.147	481.927	0.544
	206.507	41.347	479.657	406.303	553.011	0.473
	332.292	75.973	605.442	470.658	740.226	0.410
	351.176	13.551	624.326	600.285	648.367	2.445
	423.333	16.655	696.483	666.935	726.031	2.476

IV. Results and Discussion

Curve fitting was done through a process of deconvolution of glow curves into a superposition of Gaussian functions. Gaussian functions were added until a good fit was found, which was evaluated through residual analysis. The modeling process stops when residuals present a random stationary behavior around zero, and no important heterocedasticity or trends were found. Curve fitting was achieved via minimization of a least squared function.

It is important to notice that models that might fit glow curves can be obtained from many different approaches, and for each glow curve only a model is presented, and not "the" model. For instance, high degree polynomials and spline regression models as the ones presented, [11] might fit data as good as the functions used in this research—with the same interpolation problems. However, when data is deconvoluted to fit a linear superposition of functions, physical explanations can be obtained. At least, the underlying structure of the phenomena under analysis can be hypothesized by the means of the superposition principle.

In particular, Gaussian models and least squared function are not the only means to deconvolute glow curves into a superposition of functions. Kernels from many other probability functions, such as Gamma, Weibull, Gumbell, Gompetz, Lognormal, Burr and Pearson family of distributions, to name a few, can be superposed to fit glow curves. It is up to the analyst to decide which ones to use. Most of the functions mentioned are said to be flexible functions, since they are capable of providing many shapes that might facilitate the fitting of many concave functions. However, these functions, except for the Gaussian function, have their location (first moment) and spread (second central moment) coupled by their parameters. This characteristic makes Gaussian curves ideal for manual fitting at early stages of the modeling, which make the deconvolution process less dependent on complex optimizations procedures to find acceptable solutions.

Least squared functions, as said before, are not the only loss functions available to fit a linear or nonlinear function. They are one of the most popular methods in regression analysis, but they give the same weight to every error term evaluated. If heterocedasticity is present, a weighted least squared function can be used if variability can be characterized through a specific function.

Otherwise, robust regression might come in handy by taking the absolute values of the error terms instead of their squared values. Finally, if the proportion of the error with respect to the TL intensity is important for some reason, each error term within the objective function to be minimized can be multiplied by the reciprocal of the corresponding fitter value.
Many more approached can applied to fit glow curves (minimax procedure for instance), however, the least squared function used in this research is relatively simple to use, and provided an acceptable fit to the data, which makes the other approaches unnecessary at the moment.

Glow curve fitting follows a nonlinear regression analysis, which is known to struggle with optimization challenges since the loss functions usually have several local minima. It is difficult to known if the global minimum was found by the algorithm used during the optimization process. The analyst has to resign himself to obtain a decent fit, which can be evaluated via residual analysis. By the means of manual fitting, an initial solution is provided, which facilitates the search for the optimal. However, finding the best fit overall might not be the objective for an analyst, but to find a common structure of functions that can provide a physical interpretation to the phenomenon at hand. A strategy that can be explored in a future analysis of glow curve fitting is to find common structures between glow curves obtained at different doses for the same material. This might be achieved by replacing the parameters of each curve by functions of the dose. Certainly, the task is not trivial and will require higher computational power used by clever optimization algorithms, but the idea of finding a common structure instead of individual fitting for each curve seems to be worth the effort. Physical hypothesis of the underlying systems can be stated with more confidence, and interpolation could be improved in terms of precision.

V. Conclusion

In this work a method is presented step by step to make the deconvolution of Thermoluminescence glow curve for diamond thin films. With this method the number of elemental functions for deconvolution are determined systematically by minimizing the quadratic error. Each elemental function was characterized by geometrical parameters such as the translation, scale and the shape parameter. The value of each energy trap was estimated employing conventional equations and the geometrical parameters of each function. For dose above 800 Gy a second order kinetic is observed.

The stepwise deconvolution method developed during this research models glow curves independently. However, since all observations come from the same object, it should be possible to fit all curves at once by coupling the corresponding parameters with the dose level. This way, the behavior of each elemental curve within the model can be tracked over the different dose levels. As a result, deeper knowledge about the underlying structured of energy traps can be obtained.

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