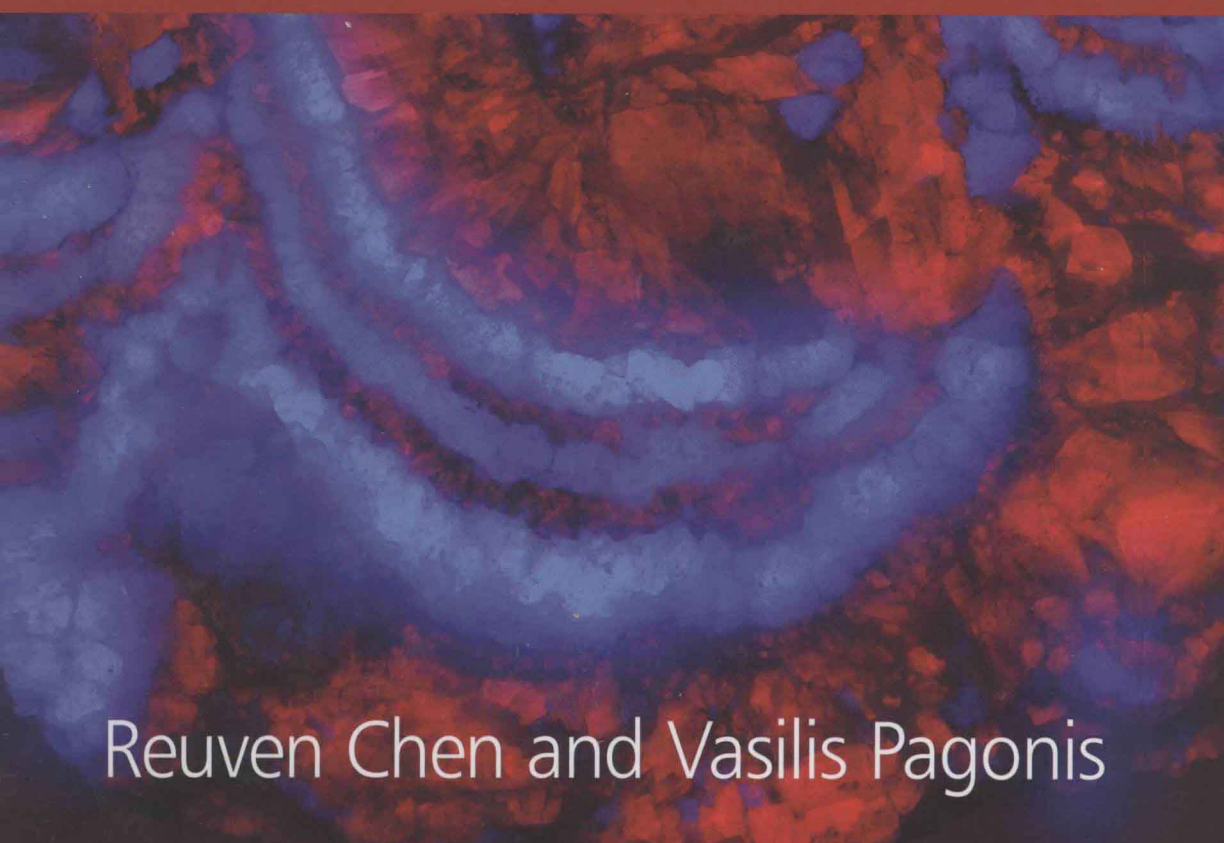
Thermally and Optically Stimulated **Luminescence**

A Simulation Approach



Reuven Chen and Vasilis Pagonis

WILEY

Thermally and Optically Stimulated Luminescence

A Simulation Approach

REUVEN CHEN

Raymond and Beverly Sackler School of Physics and Astronomy, Tel Aviv University, Tel Aviv, Israel

VASILIS PAGONIS

McDaniel College, Westminster, MD, USA

WILEY

A John Wiley & Sons, Ltd., Publication

This edition first published 2011

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Library of Congress Cataloging-in-Publication Data

Chen, R. (Reuven)
Thermally and optically stimulated luminescence : a simulation approach / Reuven Chen and Vasilis Pagonis.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-74927-2 (hardback)
1. Thermoluminescence. 2. Thermoluminescence dosimetry. 3. Optically stimulated luminescence dating.
I. Pagonis, Vasilis. II. Title.
QC479.C47 2011
612′.014480287–dc22

2010053722

A catalogue record for this book is available from the British Library.

Print ISBN: 9780470749272
ePDF ISBN: 9781119993773
oBook ISBN: 9781119993766
ePub ISBN: 9781119995760
eMobi: 9781119995777

Set in 10/12pt Times Roman by Thomson Digital, Noida, India
Printed in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire

Front cover image courtesy of Herb Yeates, http://superfluorescence.com/. Copyright (2007) with permission.

Thermally and Optically Stimulated Luminescence

About the Authors

Reuven Chen

Professor Reuven Chen is a Professor Emeritus at Tel Aviv University. He has been working on thermoluminescence, optically stimulated luminescence and other related topics over the last 48 years. Professor Chen has published approximately 170 scientific papers and two books. He has been a Visiting Professor at several universities in the USA, UK, Canada, Australia, Brazil, France and Hong Kong. At present, he is an Associate Editor of *Radiation Measurements* and referee for several international journals.

Vasilis Pagonis

Professor Vasilis Pagonis is a Professor of Physics at McDaniel College. His research involves working on modeling properties of dosimetric materials and their applications in luminescence dating and radiation dosimetry. Professor Pagonis has published approximately 70 scientific papers, as well as the book *Numerical and Practical Exercises in Thermoluminescence*, published in 2006. He currently holds the Kopp endowed chair in the physical sciences at McDaniel College.

Preface

Thermoluminescence (TL) and optically stimulated luminescence (OSL) are two of the most important techniques used in radiation dosimetry. Hundreds of papers are published every year in the scientific literature on different aspects of TL and OSL. These cover a whole spectrum of subjects, from experimental papers describing various aspects of these phenomena in different materials under different experimental conditions, many times having in mind the potential applications, to publications interested only in the dates reached by these methods and to publications on dosimetry measurements in different environments (e.g., in spaceships). On the other side of the spectrum, one can find work on the physical basis of TL and OSL, in which researchers try to obtain better understanding of the underlying processes. These include the dose dependence of the effects (which may be linear or nonlinear), possible dose-rate dependence, the stability of the effects at ambient temperature (which may include normal and anomalous fading), the dependence of these effects on the relevant defects and impurities, and the nature of the emission spectrum.

The theoretical work on TL and OSL consists, in most cases, of the study of the simultaneous differential rate equations governing the transitions of charge carriers, usually electrons and holes, between the different trapping states associated with impurities and defects in the studied sample, and the conduction and valence bands. These equations are not linear and therefore, in most cases, cannot be solved analytically. In many cases, approximations concerning the trapping parameters and functions are made to reduce the complication, and explicit equations for simplified models such as the first- and second-order kinetics can be written and solved analytically. Here, general solutions are reached from which one can consider how different phenomena may take place, e.g. how the signal fades with time at room temperature under first- or second-order kinetics, and to what extent these predictions agree with specific luminescence experiments for a given material. Obviously, this approach has a strong limitation since one does not know whether the assumptions made hold all along the temperature and time range of a TL/OSL measurement.

This book concentrates on an alternative approach, in which we simulate various experimental situations by numerically solving the relevant coupled differential equations for chosen sets of parameters. Using this approach, several complex situations can be demonstrated such as superlinear and nonmonotonic dose dependencies, dose-rate effects, the occurrence of abnormally high frequency factors and others. Obviously, the shortcoming of this approach is that it does not provide us with general solutions but rather with results associated with specific sets of trapping parameters. However, this kind of demonstration that certain behaviors are commensurate with our understanding of the underlying processes is of great importance. With the present availability of strong computing power and advanced numerical methods, this approach has become very popular during the past 20 years. A second approach that is emphasized throughout this book is demonstrating the possibility of obtaining analytical solutions of the systems of differential equations by using the quasi-equilibrium approximation. Numerous examples are given in which this approach

leads to exact analytical solutions which describe accurately the experimental results. This book is designed for practitioners, researchers and graduate students in the field of radiation dosimetry. It is a synthesis of the major developments in modeling and numerical simulations of thermally and optically stimulated processes during the past 50 years.

Chapter 1 is mostly a historical overview of the developments in TL and OSL dosimetry during the past 50 years, followed in Chapter 2 by an overview of the theoretical basis and several quantum aspects of luminescence phenomena, which is based on the energy-band model of solids. Chapter 3 deals with a number of basic experimental measurements relevant to the study of TL and OSL. In Chapter 4 we present the basic kinetic equations governing the TL process, including simple kinetic models based on first- second- general- and mixed-order kinetics. In addition, some aspects of localized versus delocalized electronic transitions during the luminescence process are discussed. The basic methods of evaluating kinetic parameters in TL and OSL experiments are the main topic of Chapter 5, and Chapter 6 addresses a variety of physical phenomena commonly encountered during TL and OSL measurements. The basic theoretical aspects and experimental techniques used in OSL dosimetry are presented in Chapter 7, with a specific emphasis on the relationship between the various models used in obtaining OSL data (LM-OSL, CW-OSL, pseudo LM-OSL, etc.). Chapter 8 addresses a topic of prime importance for radiation dosimetry researchers, namely the dose dependence of TL/OSL signals. Different types of experimentally observed dose behaviors are examined using both an analytical approach and approximate expressions obtained using certain approximations. The topic of TL and OSL simulations for dating applications is presented in Chapter 9, including simulations of recent major developments in TL/OSL dating protocols. Chapter 10 examines the use of several alternative methods for evaluating trapping parameters, based on a variety of advanced numerical methods like Monte-Carlo techniques, genetic algorithms and advanced curve-fitting methods. Chapter 11 contains a more general approach to thermally stimulated phenomena, and several methods of analyzing simultaneous thermal measurements are presented. The processes of thermally stimulated conductivity (TSC), thermally stimulated electron emission (TSEE), optical absorption (OA) and electron spin resonance (ESR) are briefly discussed, in particular in cases where their simultaneous measurements with TL can produce additional information and can be simulated along with the simulation of TL. Chapter 12 deals with applications of luminescence in medical physics and Chapter 13 with the associated phenomenon of radiophotoluminescence. Chapter 14 summarizes theoretical developments and simulation results on the effects of ionization density on TL response, which is a topic of major interest in radiation dosimetry for particles of varying ionization density. Finally Chapter 15 presents various numerical approaches to the exponential integral which appears commonly in TL applications. In addition to the comprehensive list of references, covering all the subjects discussed in the book, we have also included a list of books and review articles published in the literature from 1968 onwards. Finally, in Appendix A, we present some simple examples of computer code that simulate three important models which appear frequently in the book, namely, the one trap-one recombination center (OTOR) model, the interactive multiple trap system (IMTS), and the widely used Bailey model for quartz.

Acknowledgements

We thank our wives Shula Chen and Mary Jo Boylan for their patience, encouragement and sound advice during the years of writing this book. We would like to thank also Dr John L. Lawless for his contributions to some of the analytical aspects discussed in the book. Thanks are also due to Dr Doron Chen for important technical help in preparing the manuscript.

Reuven Chen and Vasilis Pagonis

I would like to thank all my research collaborators, students and friends in the luminescence community for their helpful contributions and stimulating discussions during the development of various luminescence models over the years. Special thanks among these are due to Dr George Kitis of Aristotle University in Greece for his friendship and extensive collaboration over the last 10 years; Dr Ann Wintle for teaching me the importance of seeking perfection in the preparation of manuscripts; to my colleagues Andrew Murray, Mayank Jain and Christina Ankjærgaard in Denmark for their hospitality and many stimulating conversations; and last but not least, special thanks to my co-author, good friend and luminescence mentor Dr Reuven Chen, for teaching me the importance of accuracy and precision during luminescence modeling work.

Vasilis Pagonis

Contents

1

Introduction

In this introductory chapter we first provide an overview of the physical mechanism involved in thermoluminescence (TL) and optically stimulated luminescence (OSL) phenomena, followed by a brief historical review of the development of TL and OSL dosimetry. This is followed by a section on the parallel development of luminescence models for TL/OSL phenomena during the past 50 years.

1.1 The Physical Mechanism of TL and OSL Phenomena

The phenomenon of phosphorescence seems to have been discovered first by Vincenzo Casciarolo (see e.g., Arnold [1]), an amateur alchemist in Bologna in 1602 who discovered the "Bologna Phosphorus", the mineral barium sulfide, which was glowing in the dark after exposure to sunlight. An account was later published by Fortunio Liceti in "Litheosphorus, sive de lapide Bononiensi lucem", Utino, 1640. In 1663, Robert Boyle gave the Royal Society one of the first accounts of TL. He described some experiments he had carried out on a diamond, saying "I also brought it to some kind of glimmering light, by taking it into bed with me, and holding it a good while upon a warm part of my naked body" (see e.g. Heckelsberg [2]). The phenomenon of TL had been known since the 17th century, and has been studied intensively since the first half of the 20th century. For example, in 1927, Wick [3] reported on the TL of X-irradiated fluorite and other materials. In 1931, she reported [4] on TL in calcium sulfate doped by manganese and fluorite, following their exposure to radium. She also described the effect of applying pressure on the TL properties of the samples. A preliminary qualitative explanation of the occurrence of TL, based on the band theory of solids was given by Johnson [5] only in 1939. The first quantitative theoretical account based on the model of energy bands in crystals, was given in 1945 in a seminal work by Randall and Wilkins [6]. Basically, TL consists of the excitation of an insulator, usually by ionizing radiation but sometimes by non-ionizing radiation or other means, followed by a "read-out" stage of heating the sample and measuring the light emitted in excess of the

Thermally and Optically Stimulated Luminescence: A Simulation Approach, First Edition. Reuven Chen and Vasilis Pagonis.

"black-body radiation". In the OSL method, discovered significantly later, the read-out stage consists of releasing the charge carriers, previously excited by irradiation, by illumination with light of an appropriate wavelength; the incident light is capable of releasing trapped charge carriers at the ambient temperature.

The understanding of the phenomenon is associated with the energy-band theory of solids, and has to do with the trapping of charge carriers in the forbidden gap states associated with imperfections in the crystalline material, be it impurities or defects. The trapping states are entities that can capture either electrons or holes during the excitation period and during the read-out stage which, in the TL process is the time when the sample is heated and measurable light is recorded. The energy absorbed during the excitation period causes the production of electrons and holes, which may move around the conduction and valence bands, respectively, and get trapped in electron and hole trapping states. Some of these traps may be rather close to their respective bands, electrons to the conduction band and holes to the valence band, so that within the temperature range of the subsequent heating, they may be thermally released into the band. These entities are usually called "traps".

The trapping states which are farther from their respective bands, in which a recombination of trapped charge carriers and mobile carriers of the opposite sign may take place are usually termed "recombination centers" or just "centers". Thus, during the read-out stage charge carriers, say electrons, may be thermally elevated into the conduction band, where they can move around before recombining with the opposite-sign carriers, say a hole, and emit at least part of the previously absorbed energy in the form of photons. However, some of these recombinations may be radiationless, meaning that the produced energy turns into phonons. It is also possible that recombinations produce photons in a spectral range which is not measurable by the device being used, and for the purpose of our analysis of the results, may be considered as being radiationless.

Note that, although very often one discusses the TL/OSL process as being related to the thermal or optical release of trapped electrons and their subsequent recombination with holes in centers, the inverse situation in which the mobile entity is the positive hole which moves in the valence band and then recombines with a stationary electron in a luminescence center is just as likely to occur. One should also mention the possibility of localized transitions, a situation where the hole and electron trapping states are located in close proximity to each other, and the radiative process takes place by thermal or optical stimulation of one kind of carrier into an excited state which is not in the conduction/valence band, and its subsequent recombination with its opposite-sign companion.

1.2 Historical Development of TL and OSL Dosimetry

The two most important applications of TL and OSL are in the broad fields of radiation dosimetry and geological/archaeological dating. In this section we present a brief outline of the historical development of luminescence techniques in these two broad application areas.

Although the first theoretical work, by Randall and Wilkins and later by Garlick and Gibson was published in the 1940s, the first practical applications of TL were suggested in the 1950s. The applications of TL in radiation dosimetry were initiated in the early 1950s by Daniels [7, 8] who also suggested that natural TL from rocks is related to radioactivity from

uranium, thorium and potassium in the material. Later, Kennedy and Knopf [9] discovered natural TL emitted from samples of ancient pottery, which led the way to the work on TL dating of archaeological samples which was developed quickly in the 1960s, first in Oxford by Aitken and his group [10] and later, in dozens of laboratories all over the world. The possible use of optical stimulation instead of thermal stimulation for evaluating the absorbed dose in a sample for dosimetry purposes was first suggested by Antonov-Romanovsiĭ [11] in the mid 1950s and mentioned later by a number of researchers who referred usually to infra-red stimulated luminescence (IRSL). The use of OSL for archaeological and geological dating was suggested in 1985 by Huntley *et al.* [12], and it has been in use in many laboratories since then.

Since the 1950s there has been a continuous extensive search for the "perfect" thermoluminescent dosimetric (TLD) material that will exhibit the ideal linear response over the widest possible range of doses, high sensitivity, excellent reproducibility and stability of the luminescence signal. The historical development, properties and uses of various TLD materials have been summarized in some detail in the book by McKeever *et al.* [13]. The use of TL as a radiation dosimetry technique was first suggested by Farrington Daniels and collaborators at the University of Wisconsin (USA) during the 1950s. Daniels *et al.* [7, 8] first used LiF for radiation dosimetry during atomic bomb testing, and they also studied and considered $CaSO_4$:Mn, sapphire, beryllium oxide and CaF_2:Mn as possible TL dosimeters during the same decade. In the 1960s a variety of new materials were also studied, namely CaF_2:Dy, $CaSO_4$:Tm, $CaSO_4$:Dy, CaF_2 and LiF:Mg,Ti. The latter material eventually became one of the most commonly used TLD materials. In the next 20 years various forms of Al_2O_3, CaF_2 and LiF were developed and considered as TLD candidates. Other commonly used and studied TLD materials are Al_2O_3:C and LiF:Mg,Cu,P. The most common applications of TLD materials are in monitoring of personnel radiation exposure, in medical dosimetry, environmental dosimetry, spacecraft, nuclear reactors, mineral prospecting, food irradiation, retrospective dosimetry, and in geological/archaeological dating.

Kortov [14] recently summarized the current status and future trends in the development of materials for TL dosimetry. This author listed the main requirements for practical use of TL dosimeters as: a wide linear dose response, high TL sensitivity per unit of absorbed dose, low signal dependence on the energy of the incident radiation, low signal fading over time, the presence of simple TL curve, luminescence spectrum matching photomultiplier (PM) tube response and appropriate physical characteristics. The author listed the useful dose range and thermal fading properties of the following seven main practical dosimetric materials: LiF:Mg,Ti (TLD-100), LiF:Mg,Cu,P (TLD-100H), ^{6}LiF:Mg,Ti (TLD-600), ^{6}LiF:Mg,Cu,P (TLD-600H), CaF_2:Dy (TLD-200), CaF_2:Mn (TLD-400), and Al_2O_3:C (TLD-500). Kortov [14] also discussed the intrinsic luminescence efficiency η of TL materials; he specifically attributed the high sensitivity of several dosimetric materials to the efficient trapping/detrapping/excitation mechanisms associated with the presence of F-centers.

In a recent comprehensive review of luminescence dosimetry materials Olko [15] summarized the progress of luminescence detectors and dosimetry techniques for personal dosimetry and medical dosimetry. The author discussed traditional personal dosimetry based on OSL, TL and radiophotoluminescence (RPL), and also reviewed more novel luminescence detectors used in clinical dosimetry applications such as radiotherapy, intensity modulated radiotherapy (IMRT) and ion beam radiotherapy. The major advantages of

luminescence dosimeters were summarized as: high sensitivity measurement of very low doses, linear dose dependence, good energy response to X-rays, reusability, and sturdiness. However, the review also recognized the problem of decreased response with increasing ionization density of the radiation field. This problem may lead to underestimation of dose after heavy charged particle irradiation. Personal dosimetry is also used widely in the medical sector, with dosimetric films gradually being replaced by TLD, OSL and RPL materials.

The pros and cons of using OSL versus TLD dosimeters have been summarized in McKeever and Moscovitch [16]. Some of the advantages of OSL dosimeters are high efficiency and stable sensitivity, better precision and accuracy, fast read-out, and no thermal annealing steps. However, TL dosimeters have the advantages of high sensitivity, no light sensitivity, simple automated read-out, possibility of neutron dosimetry, and flat photon energy response.

Olko [15] also summarized some newer developments in luminescence detectors: development of a personal neutron dosimeter based on OSL [17], laser-scanned RPL glasses used to measure the dose from fast neutrons by counting tracks of charged recoil particles [18], and fluorescent nuclear track detectors (FNTDs) which allow imaging of individual tracks of heavy charged particles [19, 20]. Oster *et al.* [21] suggested the possibility of using standard LiF:Mg,Ti (TLD-100) and a combined TL/OSL signal to increase the efficiency of detecting high linear energy transfer (LET) particles. Additional novel techniques include the development of a laser-scanned OSL system and TLD systems with a charge-coupled device (CCD) camera [22–24]. Olko [15] identified three active areas for research in new luminescence detectors, namely developing new materials for the medical field, for materials to be used in dosimetry of high LET radiation, and for materials mimicking the radiation response of biological systems. However, this author also identified the absence of luminescence detectors for neutron dosimetry as a major gap in luminescence dosimetry.

The second broad area where TL and OSL dosimetry have found extensive practical applications is in the field of geological and archaeological dating. In a comprehensive review article, Wintle [25] reviewed the historical and technological developments in the field of luminescence dating. During the time period 1957–1979, TL techniques were applied to heated materials, while in the time period 1979–1985 TL dating was extended to older sedimentary samples. The historical developments in the use of TL during this time period include the fine-grain and coarse-grain TL dating techniques, improvements in the calculation and measurement of natural dose rates, applications of TL dating to pottery and fired clay, and authenticity testing of ceramics using predose dating. During these early years, two major problems were identified which hindered successful application of TL dating: the problems of anomalous fading exhibited, e.g., by feldspars; and the phenomenon of supralinearity during dose response measurements. However, there were many attempts to extend the use of TL signals in the study of other materials, such as heated stones, calcite deposits and burnt flint. In many of these areas, TL continues to be a valuable dating tool. Starting in 1979, researchers began exploring the possibility of using TL dating techniques for determining the time of deposition of quartz and feldspar grains. The exploration of new luminescence signals during the period 1979–1985 for the dating of sediment deposition led to the next major phase in luminescence dating, which continues today. During the last 25 years, research in luminescence dating has undergone a dramatic shift, due to the discovery of new luminescence signals which could be zeroed by exposure to sunlight. These new signals led to the development of OSL dating techniques. In 2008, Wintle [25] identified

1999 as the seminal year in which the single aliquot regenerative (SAR) dating procedure was developed; this technique has revolutionized luminescence dating, by providing an accurate and precise tool for routine measurement of equivalent doses. Furthermore, the SAR protocol allows for a completely automated measurement process, resulting in major improvements in the speed of data acquisition and analysis. As a result of these major developments during the past 25 years, OSL has become arguably the most accurate and precise luminescence dating tool in Quaternary geology, as well as a valuable archaeological tool [26].

1.3 Historical Development of Luminescence Models

In this section we present a historical overview of the development of luminescence models, which took place in parallel to the historical development of experimental TL and OSL techniques described in the previous section.

Randall and Wilkins [6] wrote a differential equation governing the TL process and discussed the properties of its solution, by assuming that retrapping is negligible and that the rate of change of trapped carriers is proportional to the concentration of these trapped carriers (first-order kinetics). Garlick and Gibson [27] showed that under different relations between the retrapping and recombination probabilities, the rate of change of the concentration of trapped carriers is proportional to the square of this concentration, i.e. the kinetics is of second order. They wrote the relevant differential equation and studied the properties of its solution. Following a previous suggestion by Hill and Schwed [28], May and Partridge [29] extended this treatment to "general-order" kinetics, namely, cases in which the rate of change of the concentration of trapped carriers is proportional to a non-integer power of their concentration. Although heuristic in nature, the approach has been rather popular in the study of TL. A milestone in the development of luminescence models is the work by Halperin and Braner [30], who introduced a more realistic presentation of a single TL peak. They wrote three simultaneous differential equations governing the traffic of carriers between a trapping state, the conduction band and a recombination center. Since these equations cannot be solved analytically, Halperin and Braner [30], Levy [31] and other authors made some simplifying assumptions, which enabled the solution of the problem in a relatively easy way for some specific circumstances. It is obvious, however, that the only route to follow more complicated cases is by solving numerically the relevant simultaneous differential equations.

During the past 50 years numerous kinetic models have been published which attempt to explain various experimentally observed behaviors in luminescence phenomena. Perhaps the best overview of these models is the paper by McKeever and Chen [32] and the textbook by Chen and McKeever [33]. The approach used in the majority of published TL/OSL papers is to solve numerically the relevant simultaneous differential equations. With modern available software, this is a relatively easy task. One can use reasonable sets of trapping parameters and find how the TL, as well as OSL, signals behave. The obvious disadvantage is that it is usually very hard to draw general conclusions from the simulation. It is possible, however, to demonstrate that certain effects are compatible with specific assumptions concerning the relevant trapping states. For example, nonlinear dose dependencies of TL and OSL have been reported in some materials; even within the one trap-one