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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

“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 $\text{CaSO}_4:\text{Mn}$, sapphire, beryllium oxide and $\text{CaF}_2:\text{Mn}$ as possible TL dosimeters during the same decade. In the 1960s a variety of new materials were also studied, namely $\text{CaF}_2:\text{Dy}$, $\text{CaSO}_4:\text{Tm}$, $\text{CaSO}_4:\text{Dy}$, CaF_2 and $\text{LiF}:\text{Mg},\text{Ti}$. 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 $\text{Al}_2\text{O}_3:\text{C}$ and $\text{LiF}:\text{Mg},\text{Cu},\text{P}$. 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: $\text{LiF}:\text{Mg},\text{Ti}$ (TLD-100), $\text{LiF}:\text{Mg},\text{Cu},\text{P}$ (TLD-100H), $^6\text{LiF}:\text{Mg},\text{Ti}$ (TLD-600), $^6\text{LiF}:\text{Mg},\text{Cu},\text{P}$ (TLD-600H), $\text{CaF}_2:\text{Dy}$ (TLD-200), $\text{CaF}_2:\text{Mn}$ (TLD-400), and $\text{Al}_2\text{O}_3:\text{C}$ (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

recombination center (OTOR) model, called by Levy [31] General One Trap (GOT), nonlinear dose dependence can be expected under certain conditions. In addition, different kinds of such nonlinearity can be explained by taking into consideration the occurrence of competitors, the transitions into which are nonradiative. In some extreme cases, this behavior can be shown analytically, but the variety of nonlinear dose dependencies can be demonstrated by simulation through numerical solution of the relevant equations. The simulation should be performed for the excitation stage and for the read-out stage, and properties of the solution can be compared with the experimental results. A comprehensive approach should, however, include both the excitation and read-out stages, with a certain relaxation period in between.

The review article by McKeever and Chen [32] addressed several important questions on the usefulness and need for modeling and numerical simulations of luminescence phenomena. These authors emphasized that one of the most important purposes of modeling is to provide researchers with “a feeling of security”; the use of models can indeed improve our basic understanding of the physical processes being studied. In another familiar example, modeling can provide fundamental answers about the validity of the complex modern protocols used during luminescence dating. In the same review paper, the authors provided a critique of modeling efforts and emphasized the need to test the actual behavior of the proposed models, in order to ascertain what behaviors are possible (or not) within the model. They also pointed out that often, modeling efforts lead to the development of ad hoc models, without regard to how well the model can describe other behaviors observed in the same material. It is our belief that to some extent these two criticisms of modeling efforts have been addressed during the past 20 years, with the development of comprehensive models for a variety of dosimetric materials. As an example of such comprehensive modeling efforts, we mention the recent development of comprehensive models for quartz by several authors [34–36]. Such models have proved to be very useful indeed for explaining a wide variety of experimental behaviors in quartz. As a second example of a comprehensive model, we mention the various models developed to explain the TL and OSL properties of the widely used dosimetric material $\text{Al}_2\text{O}_3:\text{C}$. Several of these comprehensive models have been shown to be able to describe simultaneously a wide variety of TL/OSL phenomena in this important dosimetric material [37–39].