Chapter 2

Thermoluminescence

2.1 Introduction

The phenomena of thermoluminescence (TL) was observed in diamond as early as 1663 by Robert Boyle, and the term was perhaps first used by Wiedemann 1903 while explaining his observations on luminescence of fluorite (Nambi 1975). TL materials are used in many applications, most of them in the area of radiation measurement and radiation protection. The use of these materials is basically to detect ionizing radiation such as X-rays, gamma rays, alphas, betas and neutrons, but the attention of using this material to detect nonionizing radiation such as laser and UV light recently started, probably in the last three decades, at the beginning of 1970s. Few workes have carried out before 1970 to study the probability to use TL materials in UV dosimetry, unfortunately these works are not continued, and there is a long period and a gap between these studies.

2.2 Luminescent and trap center

All lattice of crystal contains defects of various kinds, and these play an important role in the thermoluminescence process. There are three categories of lattice defects:

- 1. Thermal or intrinsic defects (vacancies)
- 2. Extrinsic defects or substitution impurity ions
- 3. Radiation induced defects.

The role of defects in the TL process can be explained by the energy band model.

An energy band diagram, as shown in figure (2.1), may represent the energy band structure for an ideal crystal.

The valence band is representative of all electrons held in bound states. And the conduction band is representative of all electrons in unbound states which are free to migrate through the crystal lattice. These two bands are separated by a gap called the forbidden gap.

In this energy band model, it is assumed that E represents an electron trap center or a negative ion vacancy (alpha-center), the H represents a hole trap center and L represents a luminescence center where electrons and holes may recombine with photon emission. Lattice defects and impurities represent these traps and luminescence centers.

When the electron is captured at a negative ion vacancy the center is called the F center. V center is a positive ion vacancy filled by a hole.

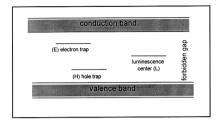


Figure (2.1): Energy band diagram for a real crystal containing defects

2.3 A general model for thermoluminescence

Thermoluminescence phenomena can be explained in three steps using energy band model as shown in figure (2.2). When ionizing radiation is absorbed in the material, free electrons are produced. The electrons will be transferred from the valence band to the conduction band. These electrons are now free to move through the crystal. If trapping levels are present, the electrons may be trapped. The production of free electrons is associated with the production of free holes that may also migrate through the crystal. The holes may be trapped also near the valence band. Many trapped electrons are unstable at room temperature. Most of these electrons return to the valence band after a very short time ($\sim 10^{-8}$ second, Chen 1981) giving rise to luminescence which can be detected during the irradiation. Some of them will be trapped in local trapping levels within the forbidden band until sufficient thermal energy is applied. Again, these released electrons will recombine with the holes at luminescence centers. The excess energy is radiated as visible or UV photons.

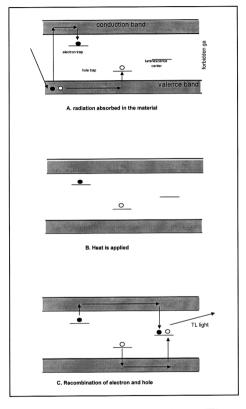


Figure (2.2): The mechanism of thermoluminescence (TL)

2.4 The glow curve

The plot of TL intensity (I) as a function of the rising temperature (T) of the TL phosphor being heated exhibits one or more peaks is termed the glow curve. The analysis of these glow curves provides information on:

- 1. Trap depth (thermal activation energy (E) corresponding to each glow peak).
- 2. Electron/hole trap densities.
- 3. Frequency factor (s).

Initially, for single glow peak, at low values of T the curve rises exponentially (where the recombination rate increases with temperature because more trapped electrons are released) and after reaching a maximum the glow peak falls down to zero as traps are depleted. Each trapping level gives an associated maximum glow peak as shown in figure (2.3). The area and peak height of each glow peak and the temperature of the T_m depend not only on the intrinsic parameters such as E and s but also on the heating rate, the radiation dose and the concentration of traps (Chen 1981). The concentration of traps in turn depends on the number of lattice defects and on the type and amount of impurity atoms present as well as on the thermal history.

2.5 Typical TL response

The plot of TL output versus absorbed dose is an important characteristic of a thermoluminescence phosphor. The typical response is illustrated in figure (2.4). It is generally appropriate to TL phosphor. At relatively low values of absorbed dose the response is linear.

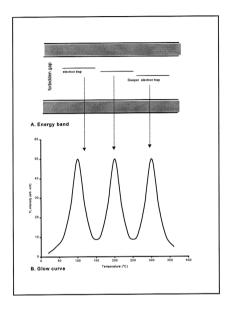


Figure (2.3): The trap depth and the glow peak

Above D_1 the response is superlinear, saturating at D_s and then falling off rapidly. The falling part is caused by radiation induced bleaching over the radiation that induced buildup.

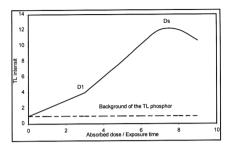


Figure (2.4): Typical absorbed dose / exposure time curve for a TL phosphor

An absorbed dose of approximately 20% less than D_s is generally taken to be the practical upper absorbed dose limit (Mckinlay 1981).

2.6 Measurement of UV radiation using TL materials

Two methods were suggested to measure UV radiation by the mean of TL materials, transferred and intrinsic method. In general, TL materials not previously exposed to gamma rays have a very low intrinsic sensitivity to UV light.

2.6.1 Transferred method

The phototransferred Thermoluminescence (PTTL) or photo stimulated thermoluminescence has been used over the years for UV dosimetry and for the dating of geological and archeaeological samples. In this method:

The TL materials are exposed to Gamma ray of known dose.

2. Annealing below 400 °C to release the trapped electron at shallow trap level.

 Exposing to UV light to release the electrons from deeper trap level and create trapped electron at shallow level.

4. The materials are heated again, and the TL intensity is usually proportional to LIV dose.

The mechanism of PTTL is shown in figure (2.5). The advantage of this method is their high sensitivity to UV radiation when compared to the intrinsic method.

LiF:Mg:Ti, CaSO₂: Tm, natural CaF₂ and BeO have been suggested for this method

2.6.2 Intrinsic method

There is no pre irradiation to gamma ray in this method. TL materials are exposed to UV light directly. The complexity of phototransferred TL posses disadvantages for practical applications in UV dosimetry. A dosimeter that responds directly to UV radiation would be more practical.

A number of TL materials have been suggested for use by this method (Mahesh et al 1989). These include, Mg₂SO₄:Tb, MgB₄O₇:Dy, AL₂O₃:Si:Ti, MgO, CaSO₂:Tm, CaSO₂:Dy and CaF₂:Dy. They show an intrinsic sensitivity to UV radiation.

2.7 Commercial TLD

Some commercial TLD have also been suggested for use in UV dosimetry. For instance, CaF₂, CaSO₄ and AL₂O₃ doped with different dopants are found to be suitable and their characteristics are discussed below:

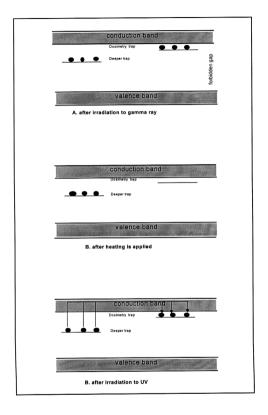


Figure (2.5): The mechanism of phototransferred thermoluminescence (PTTL)

2.7.1 CaF₂

 CaF_2 :Dy shows high intrinsic sensitivity to UV light when it is treated in air at a temperature of 900 – 1000 °C (Bassi 1975). The maximum sensitivity is about 500 times higher than that of untreated and about 10 times higher than that obtained with a gamma pre-irradiation of 0.2 krads. The glow curve is similar for CaF_2 doped with different dopants. It shows a shoulder and a peak. The fading of this material is about 30-40% when kept at room temperature for more than 250 hours (Bassi 1976). The TL intensity of terbium doped CaF_2 was the highest among the samples doped with various lanthanide elements. Even without gamma or X-ray pre-irradiation, a sintered sample of CaF_2 :Tb show high sensitivity to sunlight. The sensitivity of CaF_2 :Tb in the UVB range is very weak compared with that in the UVC range. CaF_2 :Tb phosphor sintered at 1250 °C is more useful as a TLD for sunlight UV than that sintered at 1100 °C (Fukuda 1996). It has been observed that all the CaF_2 -based TLD's exhibit an increased intrinsic UV sensitivity after temperature treatment (Pradhan 1983).

2.7.2 CaSO₄

In general, three peaks at 145, 215 and 365 °C are observed by ultraviolet irradiation of CaSO₄:Dy phosphor. The peak at 365 °C is very small and that at 145 °C fades away within a week, whereas no appreciable fading is observed for the 215 °C peak. The peak at 215 °C coincides with the gamma dosimetric peak and this peak can be used for UV exposure measurements. This dosimetric peak is linear from the detection threshold of 4 to 400 mJ cm⁻² (Vii 1993). Beyond this exposure, the

phosphor behaves superlinearly to UV exposure up to 5000 mJ cm⁻².

The TL sensitivity increases sharply by a factor of 300 as wavelength is decreased from 250 to 200 nm, and the response is negligibly small above 350 nm (Potiens 1996).

2.7.3 AL2O3:C

 AL_2O_3 :C is the most sensitive commercial TL material for non ionizing radiation in addition to ionizing radiation. Visible light does not cause the intrinsic TL but only results in severe light induced fading. UV exposure was found not to cause any significant bleaching of the TL signal of pre irradiated samples or no significant PTTL could be observed (Pradhan 1996). TL glow curve is similar for ionizing and non-ionizing radiation. The Al_2O_3 :Si,Ti phosphor was found to be insensitive to visible light, while the glow curve induced by UV light exhibits a main peak at 280 °C. This can be used for UV dosimetry from 10^2 to $5x10^4$ µJ cm² (Vij 1993)

2.8 Oxide, borate and sulfate compound phosphor

Some compound phosphor such as Gd₂O₃, Y₂O₃, MgO, BaSO₄ phosphors were suggested for UV dosimetry. The characteristic of these TL materials to UVR is shown in the following sections.

2.8.1 Gd₂O₃:Eu

The material is important in various applications such as lamps, cathode ray tubes, image amplifier tubes and other visual display devices. Recently, it was suggested

for use in solar UV dosimetry (Yeh 1996).

Gd₂O₃:Eu have been found to possess a prominent TL glow peak at 345 °C. The position of this peak depends on the total UV exposure. It is located at about 380 °C when this phosphor was irradiated by 302 nm UV at 2.4 mJ cm⁻². But it shifts to 345 °C at 19.2 mJ cm⁻². It was found that this phosphor has the highest sensitivity to the wavelength 302 nm and the lowest sensitivity to 253 nm. The linear region locates at the regions from about 3 to 250 mJ cm⁻², 1 to 10 mJ cm⁻² and 3 to 100 mJ cm⁻² for the measurement of 253 nm, 302 nm and 365 nm respectively (Yeh 1996).

The Europium (Eu) ion in the structure of Gd₂O₃ plays the role of luminescent recombination center and results in the formation of a trapping center (Su 1996).

During the irradiation the electrons could be trapped at the ion Eu³⁺ according to the equation:

$$Eu^{3+} + e^{-} \longrightarrow Eu^{2+}$$

And heating would release the holes to recombine and form exited states (Mckeever 1985) as shown in the following equation:

$$Eu^{2+} + h^{+} \longrightarrow Eu^{3+}$$

2.8.2 BaSO₄:Eu

Its intrinsic UV response is the highest amongst the available TL phosphors. The intrinsic UV response of the BaSO₄:Eu Teflon discs was 3378 times of CaSO₄:Dy (Bhatt 1997). TL fading of the exposed discs due to direct exposure to room light for 8 hours was 14 % as compared to 5 % for CaSO₄:Dy. TL glow curves both for

gamma and UV exposed BaSO₄:Eu Teflon discs are quite similar. The dosimetric peak is at 220 $^{\circ}$ C.

2.8.3 MgO

This material has strong sensitivity to UV light. The glow curve has three peaks at about 87, 144 and 190 °C. UV or ionizing radiation can stimulate the same glow peak. The UV response of these peaks is high enough to be used for the UV dosimetry. It has been observed that when the sample was exposed to UV radiation for 15 minutes and kept in the dark at room temperature for 200 hours, the first peak lost its intensity by about 20 %, while both the second and the third peaks increased about 10% (Takeuchi 1976).

2.9 Doped alkali halides

The crystal structure of alkali halides is one of the simplest. Their band gap has a wide range between 6 and 10 eV. KBr:Eu²⁺, KCl:Eu³⁺ and NaCl:Ca(T) have been suggested to be used as ionizing and non-ionizing radiation detector (Vij 1993).

2.9.1 NaCl:Ca(T)

After exposure to UVR with energy 2.4x10⁴ J m⁻², the glow curve of the phosphor displays a well-defined peak around 167 °C along with a weaker peak at a lower temperature. Peak 2 grows with the increase in magnitude of the UV dose. Its position as well as shape remains unaltered. The intrinsic response to UV radiation is in the range 10² to 10⁴ J m⁻² (Mahesh 1989).

2.9.2 KBr:Eu3+

It is sensitive to both ionizing and non-ionizing radiation. The TL glow curve of UV-irradiated samples is composed of six peaks located at 337, 384, 402, 435, 475 and 510 K. Peak 3,4,5 and 6 are more sensitive to non-ionizing radiation.

Peaks 3 and 6 are more suitable for UV dosimetry due to their high TL intensity and stability (Melendrez 1996).

2.9.3 KCl:Eu3+

It is suitable for dosimetric application for ionizing and non-ionizing radiation. The TL glow curve structure is very similar for any type of radiation with differences only in the peak intensities.

The low temperature glow peak is relatively more intense for non-ionizing radiation (230 nm) than the high temperature peak (Melendrez 1996). The dose response is linear for all types of radiation. The fading characteristic for UV irradiation seems to depend on the excitation wavelength, being stronger for wavelength around 240 nm. Because the fading was induced by external light sources, it was suggested to keep it away from surrounding light during use.

2.10 Handling technique of TL dosimeter

A complete cycle of use of a TL dosimeter consists of a combination of annealing, irradiation, storage and readout as shown in the following sections.

2.10.1 Annealing

Before performing any radiation measurement, all dosimeters should be identically annealed to standardize their sensitivities and backgrounds. The annealing may be simple but it may be complex if it is pre-irradiation annealing. Repeated annealing can reduce the sensitivity of the TL material. For example, it was found in LiF extruded-ribbon, the repeated annealing at 400 °C for 1 hour will reduce TL sensitivity up to 18% after 100 cycles (Mckinlay 1981).

2.10.2 Irradiation

This includes calibration irradiation, routine laboratory irradiation to check the stability and the sensitivity of some TL materials and measurement irradiation to determine the dose of a certain radiation.

The calibration is carried out to determine the TL response of the dosimeter to a measured exposure or absorbed dose of radiation of clearly defined energy. Sometimes the irradiation is done for a variety of reasons including checking of dosimeter sensitivities, stability, reproducibility, etc.

2.10.3 Storage and handling

Many aspects of the storage and handling of dosimeters can affect their TL sensitivity, stability, precision and the minimum detectable absorbed dose. The major effects of storage and handling of dosimeters can be divided into those due to;

 Environmental factors such as temperature, humidity, ultraviolet, visible radiation, etc.

Physical handling factors such as sieving, dispensing picking up, cleaning, sterilizing, etc.

2.10.4 Readout

TLD reader is used to read out the given dose to TL material. It is a complete system that converts TL intensity to a certain unit.

2.10.4.1 TLD reader

Harshaw TLD-reader 3500 is used to read the UV doses inside the TL chips. It has been improved several years ago. The new generations of the TLD-reader and its specifications and advantages is shown in table (2.1).

2.10.4.1.1 Manual TLD reader model 3500

The Model 3500 provides cost-effective measurements of radiation doses absorbed by single TLD element dosimeters such as ribbons (chips), rods, micro-cubes or powders. It is used in medical TLD applications and dosimetry laboratories.

The instrument includes a single element sample drawer, a linear, programmable, contact heating system and a cooled photomultiplier with associated electronics to measure the light emitted from the dosimeter during heating. TLDshell software, which runs on a separate computer, provides the user-interface and the applications software.

Specifications and advantages	TLD reader
Harshaw TLD Reader 3500	
Maximum initial investment in a TLD reader	
User-friendly for ease of operation	
Thermoelectric PMT cooler	
Automatic background subtract	表面, 尤
Harshaw TLD reader 4500	
Turnkey system for:	
Radiation Protection Applications, Research, Medical and High	
Dose	
Fully compatible with:	
TLD-REMS or NETREMS Glow Curve Analyzer & CGCD, Records Management	A Charge and in
Records Management	C Volumenta is
Harshaw TLD reader 5500	
Maximum functionality at minimum cost	
Extremely flexible parameter adjustment capability	
User-friendly for ease of operation	
Thermoelectric PMT cooler	
Automatic background subtract	
Harshaw TLD reader 6600	
 Measures beta, gamma, X-rays and neutrons singly and mixed 	
 Automatically reads a stack of up to 200, four-element cards at 70 	1 A A
cards per hour, or 240 extremity chipstrates per hour	
 Precise, closed-loop linear heating by gas Unique, high contrast display for easy reading in high or low light 	
Flexible operation with printer, with computer, or with both	
A unique chain-of custody system tracks and maintain records	
A unique chain of custody system manual and manual and	The second secon
Harshaw TLD reader 6610	
 Irradiates 204 cards per hour at 100 mR exposure 	
Overall linearity within 3%, from 30 mR to 2000 mR (0.3 mSv to	
20 mSv)	
Low radiation leakage	The second secon
Capacity: 200 dosimeters	Edward Commence of the
	Marin Comment of the Comment Marin Comment of the C

Table (2.1): Specification and advantages of TLD-readers

The general features of this TLD reader are;

- · Closed loop heating control
- · Temperatures up to 600°C
- 7 decade glow curve acquisition range
- · Optional calibration software
- · Optional high range light filter
- Suitable for all standard Harshaw TLD materials in available forms shown

The essential features common to every TLD reader is shown in Figure (2.6). It is consisted of the following major components:

1. A phosphor heating system

The prime purpose of the heating cycle is that to heat the phosphor until the electrons are liberated from the dosimetry traps.

It is often additionally used to fade rapidly any low temperature traps by means of a low temperature hold (pre-read). At high exposure levels it is often necessary to use a high temperature hold to ensure complete erasure of all electrons from dosimetry traps. A number of readers have been built utilizing heated nitrogen gas as the heat transfer medium.

2. A light collection and detection system.

The purpose of the light collection and detection system is to collect the thermoluminescence emitted by the phosphor and reject all other radiation such as infrared from the heating tray, and converting it into electrical signals.

In order to detect this small intensity of light and convert it to a current (voltage pulses), a photomultiplier tube is used in this detection system.

Photomultiplier Tubes (PMTS) are light detectors that are useful in low intensity applications such as fluorescence spectroscopy. Due to high internal gain, PMTs are very sensitive detectors. PMTs are similar to phototubes. They consist of a photocathode and a series of dynodes in an evacuated glass enclosure as shown in Figure (2.7). Photon that strikes the photoemissive cathode emits electrons due to the photoelectric effect. Instead of collecting these few electrons (there should not be a lot, since the primary use for PMT is for very low signal) at an anode like in the phototubes, the electrons are accelerated towards a series of additional electrodes called dynodes. These electrodes are each maintained at a more positive potential. Additional electrons are generated at each dynode.

This cascading effect creates 10⁵ to 10⁷ electrons for each photon hitting the first cathode depending on the number of dynodes and the accelerating voltage. This amplified signal is finally collected at the anode where it can be measured.

3. A signal measuring system

The total number of pulses corresponding to the integrated thermoluminescence emitted during the readout cycle can be counted and recorded on a pulse scaler.

4. A display and recording system

A DC amplifier amplifies the photomultiplier current and the amplified current is displayed as thermoluminescence intensity on the chart recorder or displays it on the screen.

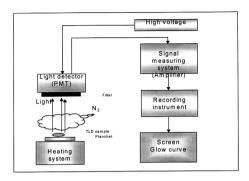


Figure (2.6): Basic component of TLD reader

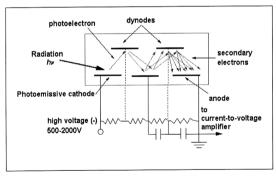


Figure (2.7): Schematic of photomultiplier tube (PMT)

2.11 Estimation of TL parameters

A number of methods were suggested to determine the trap depth (E, usually referred as the activation energy) and the frequency factors (s, the escape probability foe a single electron per second). These method include, initial rise method (Garlik and Gibson 1948), glow curve shape method, Heating rate method, phosphorescence decay analysis and curve fitting technique.

Most of these methods depend on the order of kinetic, that the possibility of electron re-traps again during heating. The advantage of initial rise method is that it does not depend on the order of kinetics.

2.11.1 Mathematical analysis

If the electrons released on heating resulting in thermoluminescence, the TL intensity is proportional to the rate of release of electrons from the traps, that is;

$$I_{TL}\alpha \frac{dn}{dt} = -pn \qquad \dots (2.1)$$

$$I_{TL} = -c\frac{dn}{dt} = -cpn \qquad \dots \tag{2.2}$$

Where n is the number of trapped electrons, c is a constant and p is the probability per unit of release of electron from the trap depth E and is given by;

$$p = s \qquad \exp\frac{-E}{kT} \qquad \dots (2.3)$$

where s is the frequency factor, T is the temperature and k is Boltzmann constant.

By substitution the value of p in equation (2.1) we get;

$$I_{TL} = -c\frac{dn}{dt} = -cns$$
 $\exp{\frac{-E}{kT}}$ (2.4)
 $-c\frac{dn}{n} = -cs$ $\exp{\frac{-E}{kT}}$ dt (2.5)
 $-c\frac{dn}{n} = -cs$ $\exp{\frac{-E}{kT}}$ $\frac{dt}{dT}dT$ (2.6)
 $-c\frac{dn}{dt} = -\frac{cs}{a}$ $\exp{\frac{-E}{kT}}$ dT (2.7)

Where B is the heating rate and is equal to dT/dt.

By integration the both sides of equation (2.7), we get;

$$-\int c \frac{dn}{n} = -\int \frac{cs}{\beta} = \exp \frac{-E}{kT} dT \dots (2.8)$$

$$Ln(n) = -\int \frac{s}{\beta} = \exp \frac{-E}{kT} dT + cons \tan t \dots (2.9)$$

When t=0, let T=T₁ (initial temperature) and n=n₀ then the constant is equal to $Ln(n_0)$, therefore equation (2.9) becomes;

$$Ln(\frac{n}{n_o}) = -\int_{\tau_o}^{\tau} \frac{s}{\beta} \qquad \exp{\frac{-E}{kT}} \qquad dT \qquad \dots$$

$$n = n_o \exp[-\int_{\tau_o}^{\tau} \frac{s}{\beta} \qquad \exp{\frac{-E}{kT}} \qquad dT] \qquad \dots$$
(2.10)

By substitution the value of n in equation (2.4), we get;

$$I_{7L} = -cn_{\sigma}s \qquad \exp{\frac{-E}{kT}} \exp{\left[-\frac{\tau}{\tau_{L}} \frac{s}{\beta} - \exp{\frac{-E}{kT}} - dT\right]} \qquad \dots \dots (2.12)$$

For low temperatures $(T \ge T_I)$ the second exponential term in equation (2.12) approaches unity.

Hence, the initial rise of the thermoluminescence intensity may be expressed by;

$$I_{TL} = -cn_o s \qquad \exp\frac{-E}{kT} \qquad \dots \tag{2.13}$$

$$Ln(I_{TL}) = (Ln(cn_o s)) - (\frac{E}{kT})$$
 (2.14)

Equation (2.14) is the basis of the initial rise method for determining E at the initial portion of the TL glow curve.

By plotting Ln (TL intensity (I_{TL})) against 1/T over initial rise region that is around the low temperature portion or a few percent of the maximum intensity of the glow peak as shown in figure (2.7) (Christodoulides 1985). The slope of straight line is (-E/k) which the activation energy E is obtained by multiplying the slope's value by Boltzmann's constant as shown in Figure (2.8).

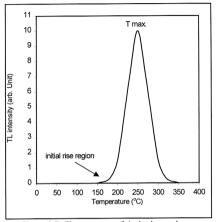


Figure (2.7): The parameters of single glow peak

The frequency factor is then calculated from the position of the maximum peak T_m using the following equation (Randall and Wilkins 1945):

$$s = \frac{\beta E}{kT_m^2} (\exp(\frac{E}{kT_m}))$$
 (2.15)

Where T_m is the temperature at the maximum peak, E is activation energy (trap depth) and β is the heating rate.

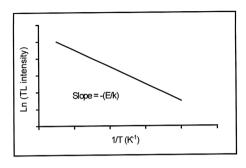


Figure (2.8): Variation of I_{TL} against 1/T