INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/750-10

"College on Advanced Techniques in Archaeometry and Conservation of Works of Art"

17 - 28 October 1994

"Thermoluminescence Dating"

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INTRODUCTION

WHAT IS THERMOLUMINESCENCE?

Thermoluminescence (TL) is a property exhibited by many insulating materials. It practically consists in a weak light emission (luminescence), during heating, as a consequence of a previous exposure to ionizing radiations. This means that, the more is the quantity of absorbed radiation, the higher will be the amount of emitted light. This phenomenon has a very low intensity and a very sensitive, especially designed instrumentation is needed to detect it.

THERMOLUMINESCENCE IN SOLIDS

Without going into mathematical details, to outline the mechanisms on which TL is based, we need to use some formalisms applied in physics to describe the behavior of electrons in solids. As a matter of fact most optical properties of solids are related to modifications of the energetic states of electrons. Typically, absorption of visible light corresponds to electrons of the absorbing medium that passes from their *normal* state (the so called *ground state*) to an *excited* state. Their return from the excited state to the original ground state is usually accompanied by emission of light (luminescence). A useful representation of the electronic energy levels in a solid is reported in Fig.1A. It refers to insulating materials in which two well defined levels can be represented: the so-called *electronic bands*, levels where the electrons are energetically allowed to move. In normal condition there are electrons only in the valence band. Absorption of some kind of energy takes electrons from the valence to the conduction band. It must be pointed out that in a perfect crystal no allowed level exists in the mid-gap between the two bands.

As outlined in the figure, light absorption corresponds to the movement of electrons from the valence to the conduction band and the subsequent return to the original levels, when occurring with light emission, is one of the many types of *luminescence*. We could say that there is luminescence every time we have the re-emission of energy from electrons that had previously absorbed it in a certain way. In the case we have just seen, the energy had been absorbed as light, and the subsequent light emission is called photo-luminescence.

Analogously we have a number of luminescences: chemi-, radio-, tribo-, bio- luminescence are some of the possible emission of light following an absorption of energy in different forms: chemical, radiological, frictional or biological, respectively. A bit more complex is the case of thermo-luminescence, where the emission of light is evidently a consequence of thermal energy absorption, but a previous energy absorption of ionising radiation is needed .

The first point to note when talking about TL is the fact that it only occurs in defective materials. As a matter of fact, however, it must be pointed out that real materials are defective: perfect crystals do not exist. Even when considering an extremely pure material, e.g. containing one impurity over one billion atoms (e.g. a concentration of 10^{-9}, or, as usually said, 10^{-3} part per million (ppm)) that material will contain about 10^{13} impurities (10 million millions) in each cubic centimetre. The presence of defects and impurities modifies the scheme of Fig.1A in the sense that new allowed levels have been introduced in the forbidden mid gap between valence and conduction bands as shown in Fig.1B. Some of these levels act as "electron traps", playing a role that is essential to the TL mechanism as it will be described in the following.

A schematic energy-level representation of TL process is reported in Fig.1B. The effect of exposure of a material to ionising radiation is mainly the absorption of energy by electrons that pass from the valence to the conduction band, analogously to what we have seen as a consequence of light absorption. The presence of trap levels allows some electrons to get *trapped*, as they are consequently called, and there remain for very long periods. The duration of these periods depends on the parameter E, that is called *trap depth*. E is in practice the quantity of energy to be given to the trapped electrons to be released and it is usually supplied as heat energy. In Fig.1B we see the consequence of heating, i.e. the thermal release of trapped electrons that are now free to move in the conduction band and afterward to recombine at *luminescent centres*, giving light emission: the TL.

We have not mentioned these luminescent centres but from Fig.1B it can be derived that they are similar to electron traps and act as their counterparts. What can be said about the physical aspect of traps and luminescent centres?

It has already been pointed out that they are related to impurities and defects. To see how they act, it is convenient to base this on the ionic crystal shown in Fig.2 though it should be realised that other types of insulator, such as covalent solids and glasses, also exhibit TL. Metals do not. An ionic crystal (e.g. calcium carbonate) consists of a lattice of positive and negative ions; however, there can be defects in this regular order such as those due to rapid cooling from the molten state, damage caused by nuclear radiation and the presence of impurity atoms. There are many types of defect that can occur, of which three simple ones are shown. A defect due to one of the negative ions being absent from its proper place, that is, a negative-ion vacancy, acts as an electron trap because the local deficit of negative charge attracts a "free" electron if it diffuses into the vicinity. Free, or "ionised" electrons result from the action of nuclear radiation in detaching them from their parent nuclei.

APPLIED THERMOLUMINESCENCE

Although TL is an interesting, very sensitive, technique to study electronic levels in solids, its increasing diffusion is mainly due to its applications in the field of radiation dosimetry.

We will see in the next chapter that the same principles that are the basis of TL dosimetry have been used to develop TL Dating.

The fact that thermoluminescent materials trap electrons as a consequence of irradiations, gives the opportunity of measuring the amount of energy absorbed by a piece of thermoluminescent material specifically treated and designed, that will be referred to as a *dosimeter.*

In practice, to realise a TL dosimeter, a suitable material must be chosen and conveniently prepared; for instance one of the most used TL dosimetric material is LiF, due to its equivalence to the human tissue (it is said to be "tissue equivalent") and its TL properties after specific "doping" with Mn or other "activators".

This last point requires some specifications: the TL properties of a material are evaluated in connection with the presence of traps and luminescent centres (see Fig.1), in order to increase its dosimetric efficiency (η) that can be defined as the amount of light emitted per unit absorbed dose:

$$\eta = \frac{\text{TL Emission}}{\text{absorbed dose}} \qquad \left[\frac{\text{photon}}{\text{Gy}} \right]$$

Gy stands for Gray and indicates the unit of absorbed dose, as it will be explained in a next chapter.

A high value of η can be reached for each trap, by increasing the concentration of both traps and luminescent centres but also other features are to be considered:

1) <u>traps</u>:

the probability ,p, of emptying each type of trap, can be described by:

$$p = \frac{1}{\tau} = s \exp \frac{-E}{KT}$$

where

τ (sec) is the lifetime of electrons in the specified trap at temperature T (in degree Kelvin);

s (sec^{-1}) is the so-called *frequency factor* and varies is the range 10^6 - 10^{10}. It is somehow related to the number of *trials of detrapping* per unit time that are experimented by the trapped electrons;

E is the depth of the trap as indicated in Fig.1;

K is the Boltzmann constant.

2) <u>luminescent centres:</u>

The electrons freed from the traps can recombine either radiatively or non-radiatively. In the latter case the only result is a small quantity of heat absorbed by the material, while in the former case light is emitted, this being a characteristic of the recombination centre. This is why *activators* are added to the material in the growing phase. The emission wavelength is typical of each activation and it is extremely important to find a wavelength that best matches the sensitivity of the detector (generally a photomultiplier type (TMP), described in the following).

To summarise what practically means *to make a TL dosimeter*:

1. A suitable material, *tissue equivalent*, must be used
2. During the growth,or after successive treatment, a high concentration of appropriate defects are generated in the material, so that stable traps are present. (Stable in the sense that can be emptied at 150°C<T<300°C)
3. Activators are added to the material, to have luminescent centres with useful emission wavelength (generally 300 nm<λ<450 nm).

The dosimeter will then be used by a person who has to control the amount of radiation which he is exposed to. To detect the absorbed dose, the dosimeter is put in a specifically designed apparatus and the emitted TL is measured and compared with the TL relative to an irradiation of known intensity.

The details about the instrumentation used to measure TL will be given when treating TL dating: in that case the very low intensity requires higher precision and sensitivity. In the case of TL dosimetry we just mention the main blocks that constitute a TL apparatus: i) a small glow oven, where the sample is put to be heated; ii) a detection system, whose main part is a photomultiplier tube (essentially a device that converts the light into an electric signal), iii) the electronic elaboration, system that processes the signal and presents the data in the form of "glow curves", see Fig. 3, where the TL intensity is presented as a function of temperature.

Radiation sources

All things, animals and human beings on earth have always been submitted to a radiation flux coming from natural origins both from outside, the cosmic rays, and from inside the earth, the natural radionuclides.

These latter are mainly Potassium 40, Uranium 238 and Thorium 232, the last two together with their decay products that are radioactive as well, so that they constitute two *radioactive family*, originating a number of alpha, beta and gamma emissions.

Together with technological development , artificial radiation sources have been added to the natural ones: X-ray apparatuses, accelerators and nuclear reactors contribute to the radiation field we are interested in measuring.

The quantity used to characterise a radioactive substance at a particular time, is its *activity*. Its unit is the reciprocal second s^{-1} and its name is the Becquerel [Bq]:

$$1 \text{ Bq} = 1 \text{ s}^{-1}$$

Due to its decay, the intensity of a radiative substance varies with time.In the case of natural radionuclides, being the decay time in the order of 10^9 years, the activity can be considered constant for relatively "short" times as are when treating historic periods (less then 10^4 years).

The interaction of ionising radiation with matter results in a transfer of energy that depends on the type of emitted particles and on the absorbing medium.

The mean energy imparted per unit mass is taken as an appropriate measure of the absorption process, the corresponding physical quantity being termed *absorbed dose*. Its unit is the Gray (Gy) that corresponds to 1 J of absorbed energy per 1 Kg of unitary mass:

$$1\text{Gy} = 1\text{J} / 1\text{Kg}$$

TL DATING

As in dosimetry we are primarily concerned with evaluation of the absorbed dose that has been received by our "phosphor", known now as the paleodose and from this the age is calculated, in principle at any rate, according to the simple relation

$$\text{Age} = \frac{Paleodose}{Dose - rate}$$

TL dating was first developed for application to pottery and in that case the TL clock is set to zero by the firing of the raw clay by ancient man; the paleodose (alternatively called *archaeological dose*) is the total dose received between this ancient drainage and measurement of the *natural TL* in the Laboratory. The *dose-rate* responsible is due to internal radioactive impurities (thorium, uranium and potassium-40) in the pottery itself and external ones in the surrounding burial soil. Typically we are dealing with a paleodose of between a few grays and a few tens of grays. The dose-rate is usually within the range 1 milligray per year to 10 milligrays per year, of which the internal contribution is from α^- and β^- radiation and the external contribution is γ radiation from a sphere of radius 0.3 metre, plus a small dose-rate to cosmic radiation - usually less than 1.5 milligray per year.

In comparing TL dating with TL dosimetry one immediate difference is that the natural "phosphors" - quartz, feldspar, calcite, etc. - are much less bright than artificial phosphors (though it should be noted in passing that natural calcium fluoride - fluorite - is as bright a phosphor as most artificial ones and superior in some other respects). Hence we talk in terms of minimum detectable doses of a few hundred milligrays rather than tens of nanograys and efficiency of light collection is a dominant consideration in apparatus design, together with special attention to the rejection of thermal radiation (i.e. red hot glow) from the sample and the heater plate; because storage times are several orders of magnitude longer than in dosimetry it is necessary to utilise deeper traps so that the glow curve usually needs to be taken to 500°C, or more, rather than 400°C. It is also absolutely vital to employ stringent precautions for the suppression of non-radiation-induced TL ("spurious"); in addition to flushing a high purity gas (such as argon or nitrogen) through the glow oven it is necessary to ensure removal of residual air from the oven by evacuating it to around 20 millitorr before admitting the inert gas.

As we shall see most natural phosphors exhibit supralinearity (see fig.4): they start off with a lower sensitivity than they have in the later linear region. Resetting the TL to zero by heating usually alters the sensitivity.

In respect of evaluation of dose-rate (or "annual dose") we have to contend with the combined effects of a mixed radiation field and inhomogeneity both in radioactivity and TL sensitivity; grain size and/or mineral separation are often necessary. Also, we must take into account the lower efficiency of α-particles in inducing TL. With sufficient care and patience the effects can be accomodated but as with supralinearity it is uncertainty about the past that brings in the real limitations. The effective dose-rate is dependent on the water contents of sample and soil; there may have been changes in climate and water table in the past. Worse still, due to percolation of ground water, there may have been movement of uranium into or out of the sample. The escape of the gaseous decay products radon (Rn-222) and thoron (Rn-220) can also interfere with accurate assessment of dose-rate. In addition there is the possibility that at t=0 the uranium chain was not in equilibrium in respect of radium-226 (half life 1600 years) and thorium-230 (half life 75×10^3 years); the later is of particular relevance in paleolithic dating.

Apparatus

As mentioned above, a dominating factor in designing measurement apparatus is the weak intensity of the TL (for a typical sample it is about 10^5 photons per second per steradian, roughly 10^{-11} lumens per steradian). Figure 5 illustrates the basic features:

(a) The solid angle of collection should approach π steradians

(b) The heating-rate should be fast (e.g. 10° to 20° C per second). The intensity of the TL is approximately proportional to the heating rate whereas photomultiplier noise and thermal radiation are independent of it. There is a practical limit to the heating rate because at high rates thermal lag in the sample becomes variable between runs.

(c) The background of thermal radiation from the sample and the heater plate on which it is carried must be minimised. The hot area "seen" by the photomultiplier should be restricted to the sample itself by a suitable mask and in addition a wavelength-restrictive colour filter (e.g. Corning 7-59 or 5-60) plus an infra-red rejecting filter (e.g. Chance-Pilkington HA3) are necessary.

(d) To eliminate spurious TL it is essential to flush the oven with high purity argon or nitrogen; usually a flow rate of several litres per minute is used. For many types of sample it is also necessary to remove residual air by pumping down to around 20 millitorr with a backing pump. When there is trouble with spurious TL the importance of prior evacuation cannot be strongly emphasised, and also of gas purity.

(e) Photon-Ratemeter System. The signal is taken from the photomultiplier anode in pulse form (each pulse corresponding to the arrival of a photon at the photocathode) and fed through a fast amplifier (with a risetime of less than 20 ns) to a pulse-height discriminator and ratemeter. The output of the ratemeter is fed to the Y axis of the coordinate plotter. This system had been found advantageous with respect to discrimination against photomultiplier noise compared with the more conventional "dc mode" of operation in which the pulses at the anode are integrated into a current which is fed to the coordinate plotter through a picoammeter or dc amplifier. The photon-ratemeter system has the additional advantage that measurement is less dependent on changes in photomultiplier and amplifier gain. The system also lends itself to feeding into a microprocessor. The main disadvantage is lack of dynamic range: "pile-up" of pulses results in serious nonlinearity of ratemeter response when rates of the order of 10^6 pulses per second are exceeded.

(f) Photomultiplier, EMI type 9635Q, has a "biakali" (K_2CsSb) photocathode. The spectral response of this falls off sharply for wavelengths in excess of 550 μm and this is a desirable characteristic in respect of reduction of the thermal radiation background signal. The dark noise is low too, typically around 100 pulses per second at room temperature, so that the trouble of cooling the photomultiplier is avoided.

Construction of the system is well within the competence of any self-respecting physics or engineering laboratory but there are in fact two suitable commercially available systems widely used in TL dating: from Littlemore Scientific, Railway Lane, Littlemore, Oxford and from Daybreak Nuclear and Medical Systems Inc., USA.

PRACTICAL PROCEDURES FOR TL DATING

Unfortunately, in practice TL dating is more complex than this simple principle might suggest. Several difficulties have to be taken into account. These difficulties can be divided into those which are caused by the TL phenomenon itself, those which are caused by the artificial irradiation and those which are introduced when evaluating the natural dose rate.

The major problems caused by the TL phenomenon are: lower TL-efficiency for α- radiation than for β- or γ-radiation, non-linear growth of TL with increasing dose (supralinearity, saturation), change of TL-sensitivity by heating (especially the pre-dose effect), spurious, i.e., non radiation induced TL, thermal and anomalous fading of TL.

The lower TL-efficiency for α- radiation than for β- or γ-radiation is the consequence of the high ionisation density along the α-tracks with saturation of the available electron traps. The ratio of TL-efficiency of α- radiation to that of β - or γ-radiation is usually expressed as the k-value. The different TL-efficiencies result in a modified, general age equation

$$t = \frac{ED_\beta}{k \times NDL_\alpha + NDL_\gamma + NDL_\beta}$$

in which ED_β is the artificial β-dose ("equivalent-dose") which produces a TL signal equivalent to the natural TL:NDL_α, NDL_β and NDL_γ are the fractional α- , β- and γ-dose rates, respectively.

Supralinearity is the increase of TL sensitivity during the first few hundred rad of radiation dose. In case of supralinearity a correction ("intercept correction") has to be applied for dating. At higher doses, around thousand Gy, the TL growth curve becomes sublinear due to *saturation* of the electron traps. Saturation generally restricts TL dating to last million years.

Often one observes a change in TL sensitivity after a sample has been heated in order to drain its TL. This difference in sensitivity between first and second glow may be due in part to the changed transparency of the sample and in part to the pre-dose effect. The pre-dose effect is the increase of sensitivity from first to second glow which depends on the magnitude of the radiation dose the sample has absorbed before heating. Regardless of its causes the sensitivity change has for dating the consequence that natural TL and equivalent dose cannot be measured on the same sample material. Instead, one needs, in principle, at least two aliquots. From the first aliquot one derives the natural TL. The second aliquot receives a known artificial dose in addition to the natural ones before one measures its TL. In this way one constructs a TL-growth on unheated sample material. In practice more than two aliquots are needed in order to check the identity of the aliquots and the linearity of the TL-growth curve.

Spurious TL may have several causes such as pressure, friction, light exposure and chemical reactions. Since a spurious TL component would increase the age one surpresses it by measuring the TL-glow under extremely pure nitrogen or argon atmosphere. On the other hand, fading of the natural TL would lower the age. Thermal fading, as well as spurious Tl, can be recognised by the plateau test. Another, not yet well understood kind of fading is the so-called "anomalous fading", which is commonly observed in feldspars and zircons. It may be detected by storing artificially irradiated sample aliquots for several weeks and comparing their TL signal with freshly irradiated aliquots.

In order to determine the k-factor and the equivalent dose on needs well calibrated radioactive sources. Usually ^{241}Am or ^{242}Cm are used as α-sources and ^{90}Sr-^{90}Y as β-source. The energy dosimetry of such sources is an extremely difficult task since it depends on many parameters such as type. size and activity of the source, the radiation geometry, the type and thickness of the target and others. Large systematic errors in dating may and do result from inadequately known sources. Lately major efforts on an interlaboratory base are made in a more accurate calibration of the sources. Literature pertinent to this aspect is given in the appendix.

When evaluating the dose rate major problems are caused by the inhomogeneous, spatial distribution of radioactivity, possible disequilibrium in the radioactive decay chains and by the absorption of radiation by the water content in the sample.

When the radioactivity is inhomogeneously distributed on scale which is comparable or larger than the range of the radiogenic particles, detailed microdosimetry considerations have to be taken into account for the dose rate evaluation. This is best explained by using pottery as an example which contains quartz grains of 100 µm diameter in a fine grained matrix of less than 10 µm diameter in a fine grained matrix of less than 10 µm grain size. All the radioactivity is contained in the matrix. the β- and γ-particles from the matrix with their average ranges of few nm and 30 cm, respectively, would penetrate the quartz grains and the matrix equally. However, the α-particles with their average range of 25 µm would only reach the outer shell of the quartz grain leaving on α-sheltered core. Therefore the α-dose received by the quartz grains would be less than that received by the matrix. This illustrates that dose rates can be evaluated only for defined grain sizes. This necessitates grain size fractionations for the dating of samples with inhomogeneously distributed radioactivity.

Radioactive disequilibrium within the decay chains is a serious set-back for TL dating. For the correct evaluation it would be necessary to know at which member within the chain disequilibrium occurs. One of the members most susceptible to disequilibrium is ^{222}Rn in the ^{238}U-chain. As a rare gas with a half-life of 3.8 days radon-222 may easily diffuse from a sample. There are several approaches to discover radon loss.

Finally, any water content in the sample and the surrounding soil may absorb radiation. In order to make appropriate corrections the natural water content has to be determined. Apart from the present moisture content also its seasonal and long-time climatic changes must be considered.

Because of the complications outlined in the previous section several dating techniques have been developed.

The quartz inclusion technique was developed for the large (compared to α-range) quartz grains in pottery. The quartz grains free of radioactivity are separated from the crushed pottery and their dose shell is etched away with hydrofluoric acid. The remaining cores of the quartz grains which are used for TL measurement have only received the β- and γ-contribution of dose from the matrix. Since also the β-dose is to some degree attenuated in coarse quartz grains a correction must be applied. However, new investigations have somewhat modified this simple picture. The quartz grains themselves may contain radioactivity and their etching rate can vary considerably among the grains. Main advantages of this dating technique are the elimination of the difficult α-dosimeter and the resistance of quartz against anomalous fading.

On the opposite, the fine grain technique uses only the matrix of the pottery below 10 μm grain size.This fraction received the full α-, β- and γ-contributions of the natural dose rate. For the artificial irradiation one needs both α-, and β- sources. Because the fine-grain matrix from archaeological ceramics contains commonly feldspar the TL of fine grain fractions is susceptible to anomalous fading. Both, the quartz inclusion and the fine grain techniques, are the standard TL dating techniques for archaeological ceramics.

REFERENCES

M. J. Aitken: "Thermoluminescence Dating", Academic Press, London 1985

M. J. Aitken: "Science-Based Dating in Archaeology", Longman, London 1990

NOTE

A new company producing TL-Dating Apparatuse~~s~~is:
AeDi, Via M.Dal Re, 6 Milano

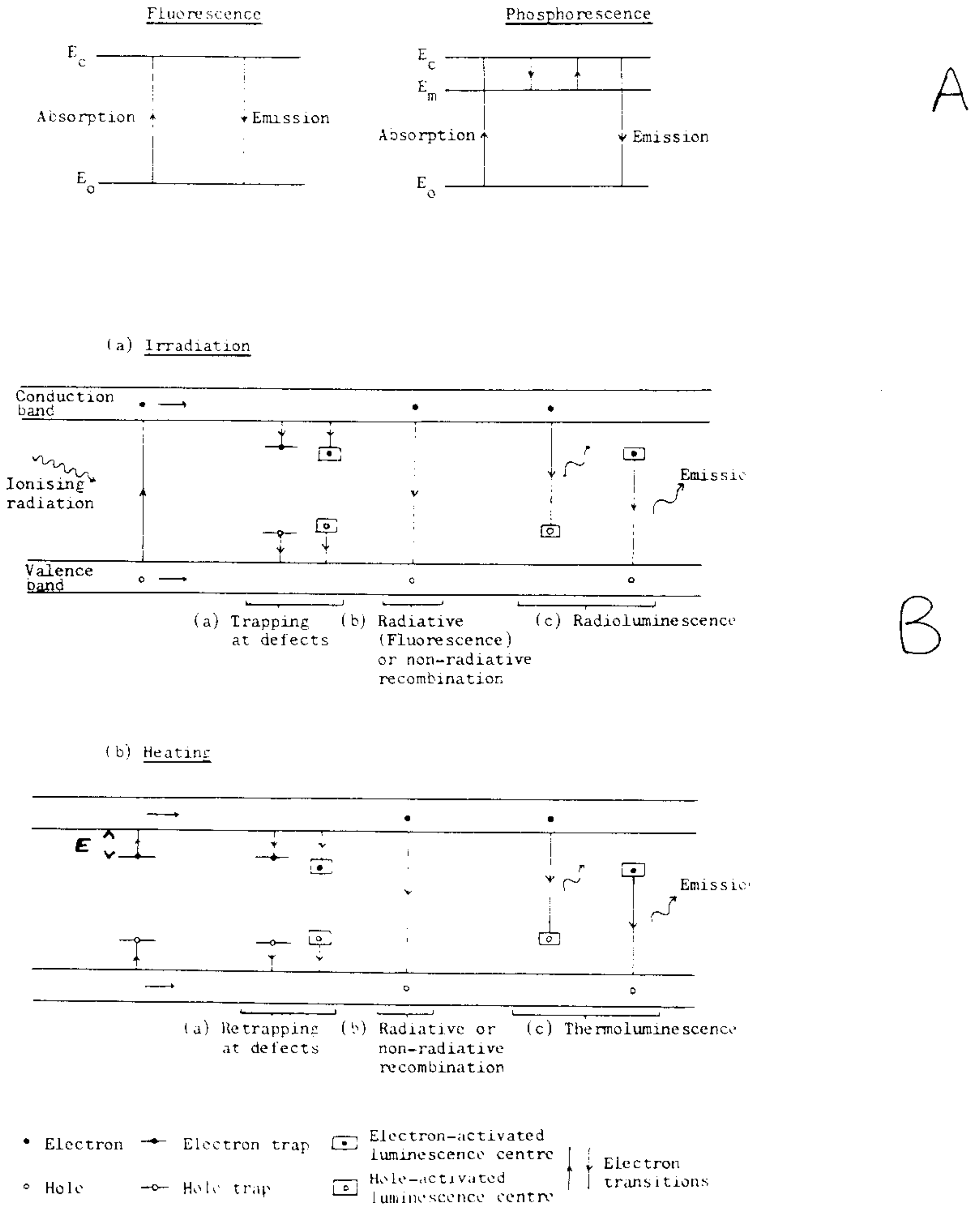
Fluorescence
Phosphorescence
E_c
Absorption
Emission
E_o
E_c
E_m
Absorption
Emission
E_o
A
(a) Irradiation
Conduction band
Ionising radiation
Valence band
Emissic
(a) Trapping at defects
(b) Radiative (Fluorescence) or non-radiative recombination
(c) Radioluminescence
B
(b) Heating
E
Emissio
(a) Retrapping at defects
(b) Radiative or non-radiative recombination
(c) Thermoluminescence
Electron
Hole
Electron trap
Hole trap
Electron-activated luminescence centre
Hole-activated luminescence centre
Electron transitions

FIG. 1

Possible Colour Centres in Alkali Halides

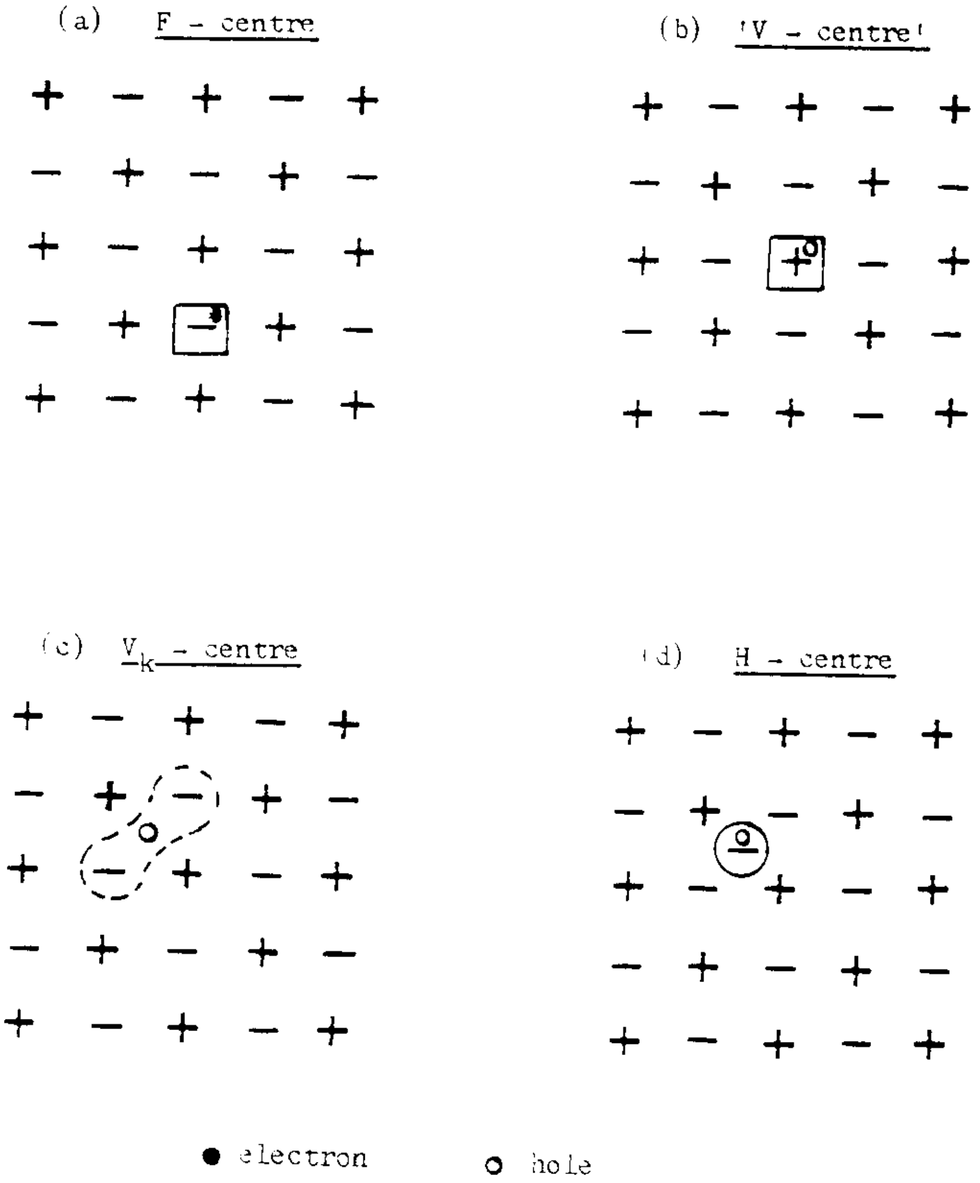

FIG. 2

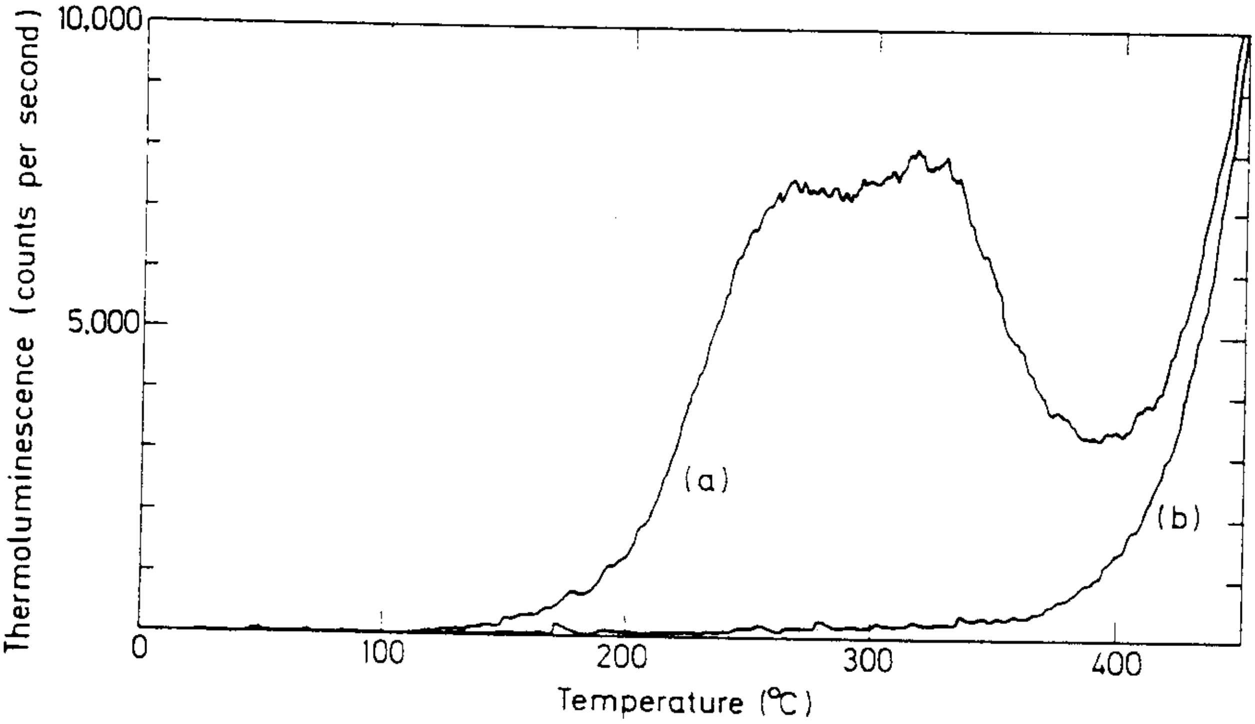
10,000
5,000
Thermoluminescence (counts per second)
0
100
200
300
400
Temperature (°C)
(a)
(b)

FIG. 3

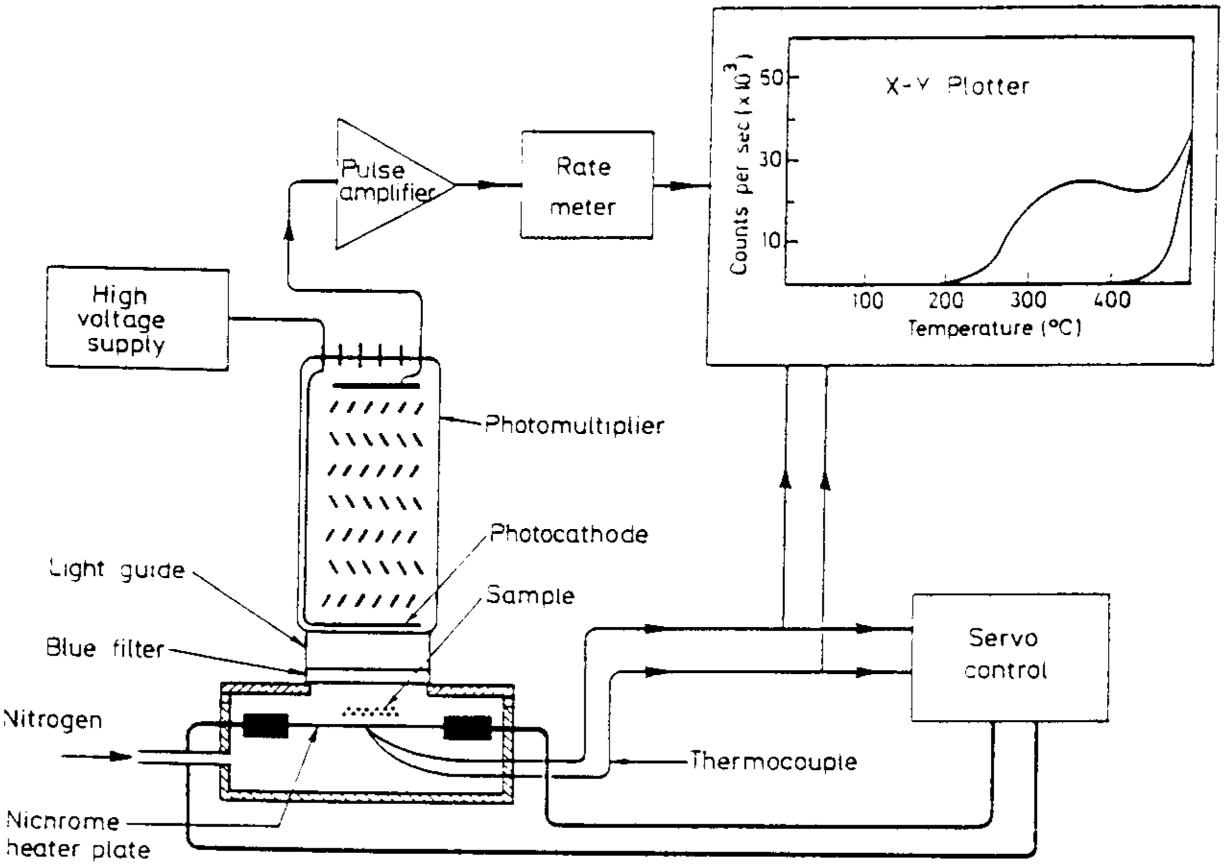
X-Y Plotter
Counts per sec (x 10^3)
50
30
10
100
200
300
400
Temperature (°C)
Pulse amplifier
Rate meter
High voltage supply
Photomultiplier
Photocathode
Light guide
Sample
Blue filter
Nitrogen
Nichrome heater plate
Thermocouple
Servo control

FIG. 4

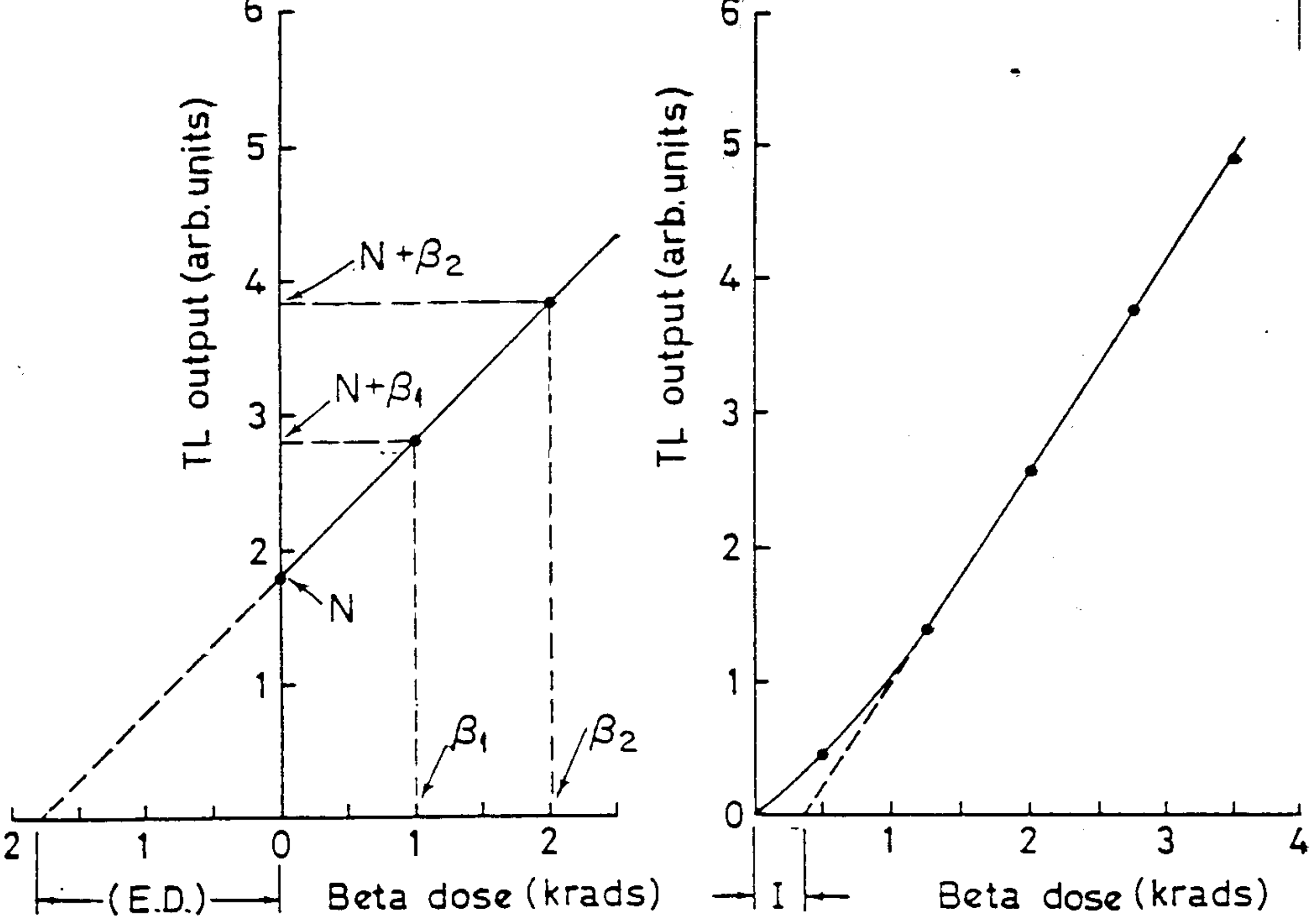
TL output (arb.units)
6
5
4
3
2
1
N + β_2
N + β_1
N
β_1
β_2
2
1
0
1
2
(E.D.)
Beta dose (krads)
TL output (arb.units)
6
5
4
3
2
1
0
1
2
3
4
I
Beta dose (krads)

FIG. 5