

Structural Factors Influencing Thermoluminescence
in Ionic Crystals

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by

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ABSTRACT

LiF single crystals have been grown with controlled Ti and Mg dopant levels. A polycrystalline LiF dosimeter has been produced from these crystals by a method of warm pressing. Both forms of the material have been characterised by ionic conductivity and microhardness measurements and chemical analysis. A thermoluminescent read-out unit was designed to monitor the radiation effect on the material. The resultant glow curves obtained have been studied with respect to the effect of magnesium concentration, heat treatment and re-irradiation. The material produced has been shown to have the same characteristics as that produced commercially. Irrespective of the form of the material increasing the magnesium concentration causes a shift to the right in the resultant glow curve, whilst repeated irradiations cause thermoluminescent enhancement. A 'one peak' phenomenon has been observed in the single crystals with a subsequent need to shield the material from daylight; the polycrystalline dosimeters do not require such treatment. Reproducible consistent results can be obtained from these dosimeters, the best results coming from a standard anneal of 400°C followed by an air cool - easy results that can be carried out without sophisticated equipment.

CHAPTER I

INTRODUCTION

The phenomenon of luminescence, that is, the absorption of energy by a substance and its re-emission as visible or near visible radiation, has been scientifically recognised for more than two centuries (1). Although Bequerel (2) had already started a systematic investigation in 1885, it was not defined by Wiedeman until 1889 (3). Five years later Madame Curie (4) described the thermoluminescent effects of ionising radiation on radium and in 1925 Wick (5) described the natural thermoluminescence of several different phosphors.

Various types of luminescence exist, for example, photoluminescence due to absorption of electromagnetic radiation, and cathodoluminescence produced by electron bombardment. Luminescence can be distinguished from thermal radiation in that the former does not follow Kirchoff's Law for absorption and emission (6).

When luminescent materials are excited, emission occurs during this excitation and in some cases for considerable periods afterwards. The emission during excitation is generally referred to as fluorescence, that which comes afterwards as phosphorescence. The exact definition of these terms has been, in the past, the subject of much discussion (7). In order to define a line of demarcation between the two the limit of fluorescence has been fixed at 10^{-8} sec order of relaxation time of an isolated gaseous ion. Phosphorescence of long duration is usually confined to crystalline solids of inorganic constitution whose luminescence is due to activation by traces of specific impurity.

1.1. Thermoluminescence in Ionic Crystals

Thermoluminescence is the emission of light produced by heating a solid to a temperature below that of incandescence. In order to exhibit this phenomenon a substance must have an ordered structure such as is found in crystals, or a semi-ordered structure as in glass. The

substance must be exposed to radiation that will produce a cloud of electrons within the lattice when radiation is absorbed. The alkali halides are a good example of such a material, and a qualitative understanding of the phenomenon can be obtained in terms of the properties of defects in the crystal. The ability to exhibit thermoluminescence in certain crystals can be produced by various types of high-energy radiations. An energy of about 10eV is sufficient to remove electrons from ions in most crystals, but unless there are traps into which the released electrons can go, there is no mechanism for thermoluminescence. To understand how these traps are formed one must examine the structure of the crystal. Several different types of electron traps can exist.

1. Imperfections and vacancies in the crystal lattice produced when the crystal is formed, or created later by mechanical methods.
2. Statistical imperfections due to kinetic motions; these increase with increasing temperature.
3. Distortions produced by impurity ions of larger or smaller charge and size than those comprising the host lattice.
4. Ion dislocations or 'holes' produced by radioactive bombardment.

A crystal may possess many trapped electrons but will only exhibit thermoluminescence on heating if a mechanism exists such that the extra energy present can be released as visible light. This process is thought to occur at certain emission centres in the lattice, either associated with impurities, as in the case of artificial phosphors and natural fluorites, or with other irregularities such as displaced lattice ions.

The role of impurities in determining the character of thermoluminescence has been extensively studied (8). Daniels *et al* (9) have shown that individual peaks in fluorite glow curves emit different colours of light, indicating that electron traps are intimately associated with particular emission centres, which have been demonstrated to be rare

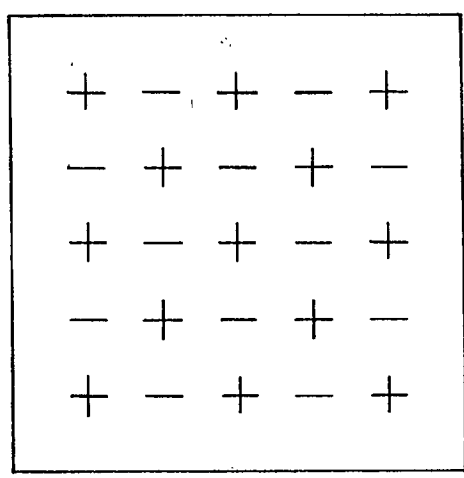
earth impurities (10). In this case it is thought the electrons are trapped in distortions produced by foreign ions.

Seitz (11) and Slater (12) have studied the production of ion dislocations in various materials by α -particles. The haloes of colour found round radioactive inclusions are thought to be due to electrons trapped in dislocations produced by the radiation.

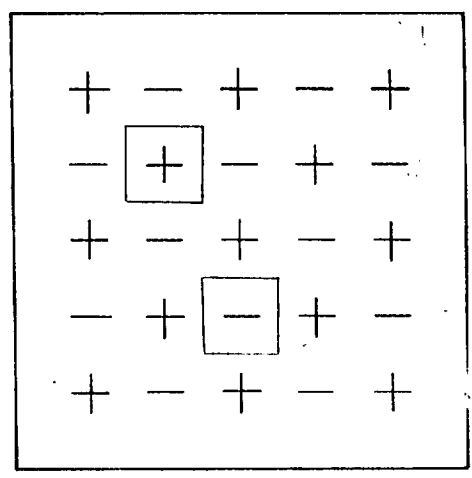
1.2. Formation of Colour Centres in Alkali Halides

The alkali halides consist of two interpenetrating cubic lattices (f.c.c.) of alkali and halide ions, Fig. 1.1. In an ideal system these would exist as uninterrupted alternating alkali and halide ions (Fig. 1.1a). However, in real systems extensive studies have shown that imperfections exist such as shown in Fig. 1.1b,c,d. The most common defect in the alkali halides is shown in Fig. 1.1b, where occasional positive and negative ions are missing at random, this is known as a Schottky defect. In order that electrical neutrality be maintained in a pure crystal, the number of alkali-ion vacancies must equal the number of halide-ion vacancies. Figure 1.1c and d illustrate other possible imperfections where an ion has been displaced from its normal lattice position into an interstitial site, leaving a vacancy behind; this is known as a Frenkel defect. The existence of Frenkel and Schottky defects have important consequences when the crystal is exposed to ionising radiation.

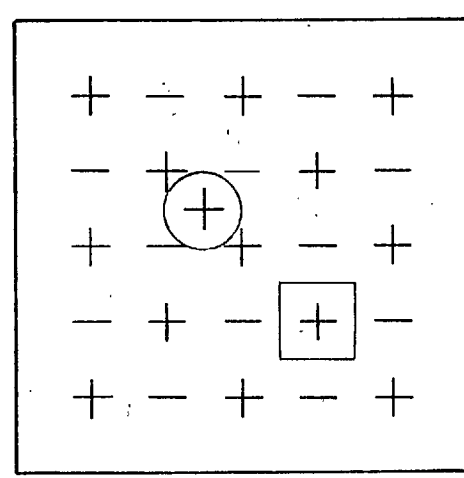
The alkali halides are insulating materials and thus according to the band theory of solids their structure must consist of a full valence band separated from an empty conduction band by a large forbidden gap (of the order of 10eV). The full valence band corresponds to the filled p-orbitals of the halide ions, the conduction band to the empty s-orbitals of the alkali metal ions. If an electron absorbs sufficient energy it can be promoted from the valence band to the conduction band. This process corresponds to the removal of an electron from a halide ion and the resulting deficiency is known as a 'positive hole'. The electron



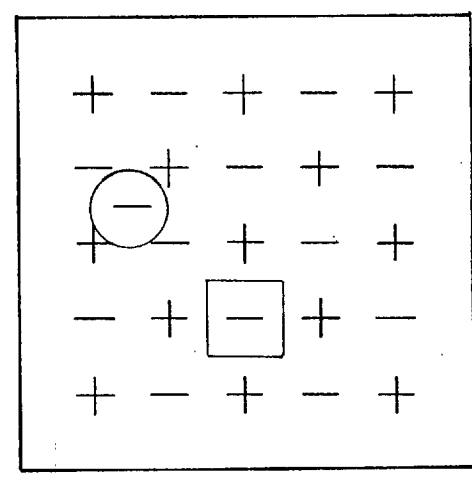
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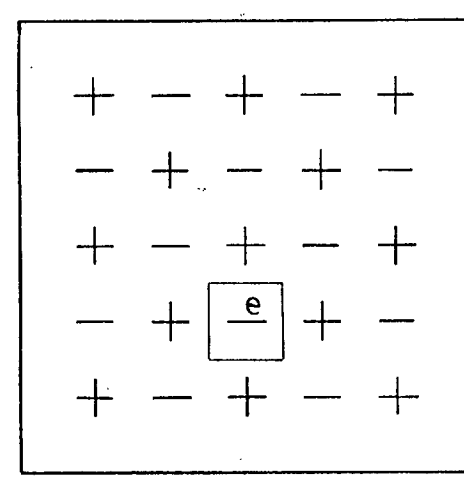
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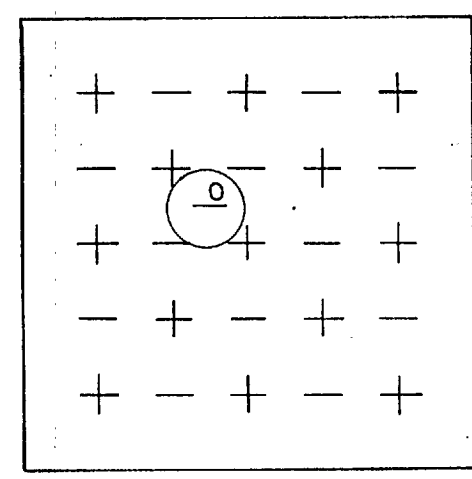
c



d



e



f

+	Alkali Ion	-	Halide Ion	e	Electron
+	Alkali-Ion Vacancy	-	Halide-Ion Vacancy	o	Hole
+	Alkali-Ion Interstitial	-	Halide-Ion Interstitial	<u>e</u>	F Centre
				<u>o</u>	H Centre

Fig. 1.1.

and hole produced in this way are free and may move independently through the crystal in the conduction and valence band respectively.

In Fig. 1.1b and d the halide ion, vacancies are regions of localised positive charge since the surrounding positive charges are not completely neutralised. If, by the action of an X-ray photon, an electron is liberated and wanders near this vacancy it will be attracted by a coulombic force and thus become 'trapped' as in Fig. 1.1e. Similarly an interstitial halide ion represents a region of excess negative charge and the 'positive hole' migrating through the crystal can become coulombically attracted as in Fig. 1.1f. In addition to liberating free electronic charges that interact with pre-existing structural imperfections, ionising radiation can also produce vacancies and interstitials in previously perfect regions of a crystal.

The centre comprising an electron trapped at a halogen-ion vacancy (Fig. 1.1e) roughly resembles a hydrogen atom in which the electron is bound by the positive proton charge. Like a hydrogen atom the electron-vacancy system has certain discrete allowed energy levels and by absorption or emission of the appropriate quanta of energy it can make transitions between these levels. The absorption of a light photon of correct frequency can raise the electron from the ground state to one of its higher states and a sufficiently energetic photon can even expel the electron from its 'vacancy trap'. The absorption of light makes the crystal coloured. The imperfections giving rise to these absorptions are therefore known as 'colour centres'. The particular centre consisting of an electron trapped at a halide-ion vacancy as shown in Fig. 1.1e is called an F-centre, and that in Fig. 1.1f an H- or more recently a V-centre. The latter is usually found when natural alkali halides are irradiated at very low temperatures. For most alkali halides, the principle F-centre absorption band lies in the visible region of the electromagnetic spectrum, and that of the V-centre lies in the near

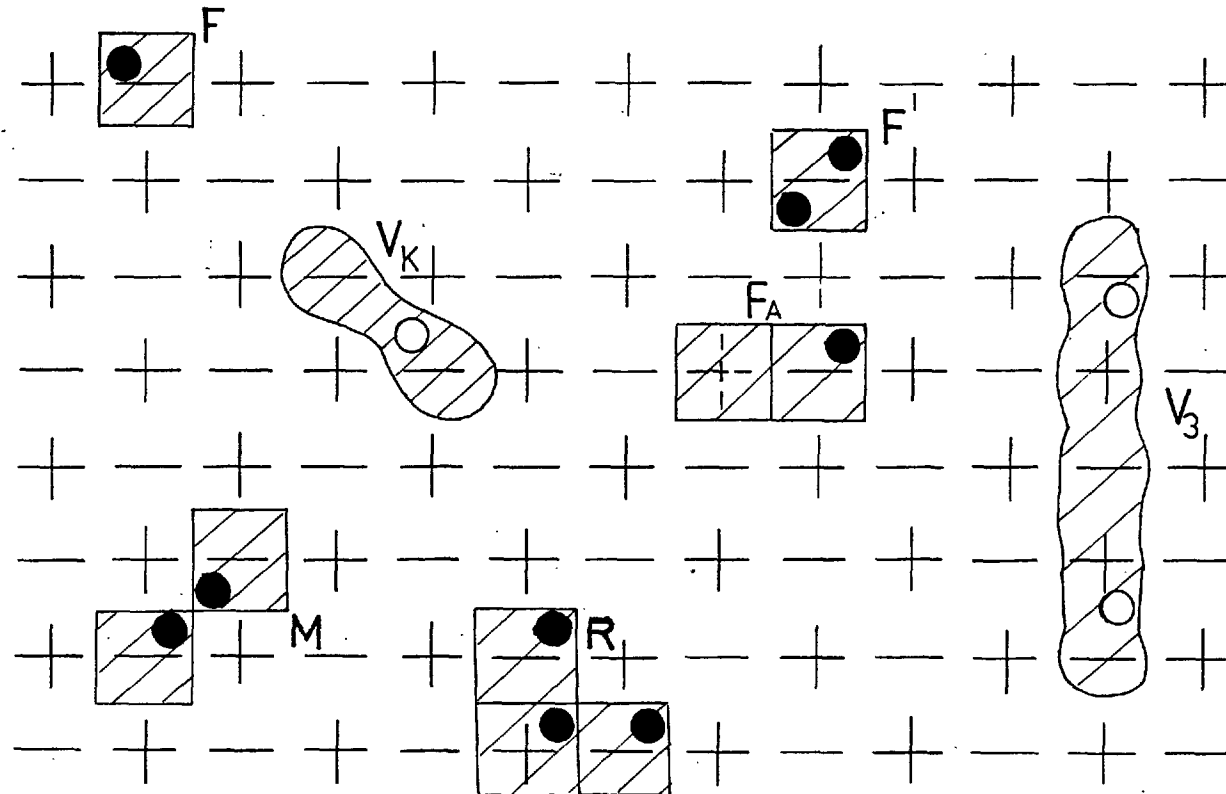


Fig.1.2.

● Electron ○ Hole $\begin{array}{c} | \\ -+ - \\ | \end{array}$ Impurity monovalent ion

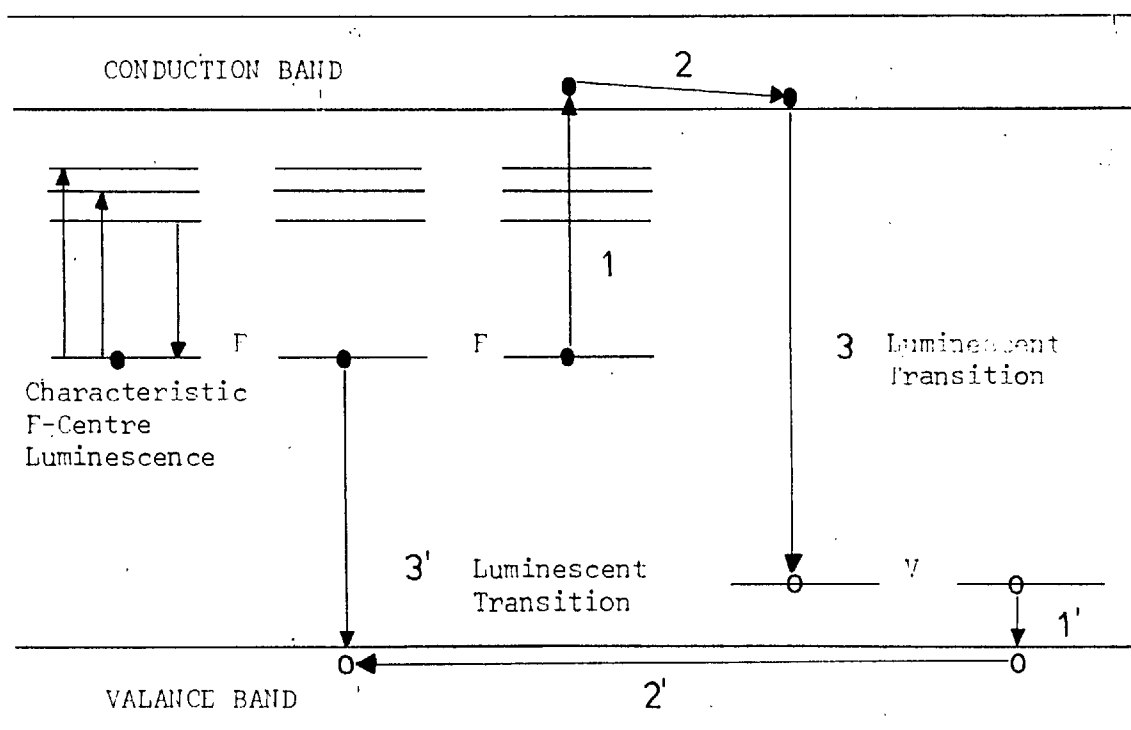
(Brown (13))

ultraviolet. Although it is well established that colouration can be removed by heating, it is not so well known that thermoluminescence usually accompanies the removal of the colour (6).

Figure 1.2 shows schematic models for a number of other types of colour centre. The F' centre can be thought of as two electrons trapped at a single anion vacancy and the F_A centre as an electron trapped at an anion vacancy adjacent to a monovalent impurity ion. The R and M centres may consist of aggregates of F centres but little agreement exists among investigators as to the correct model for them (13). The model for the V_k centre is a self-trapped hole, localised between two adjacent halogen ions which are displaced from their normal lattice sites by the inherent charge of the hole. V_3 is a multiple-hole band consisting of halogen ions which have trapped holes to form molecular halogens. (14)

1.3. Colour Centres and Thermoluminescence

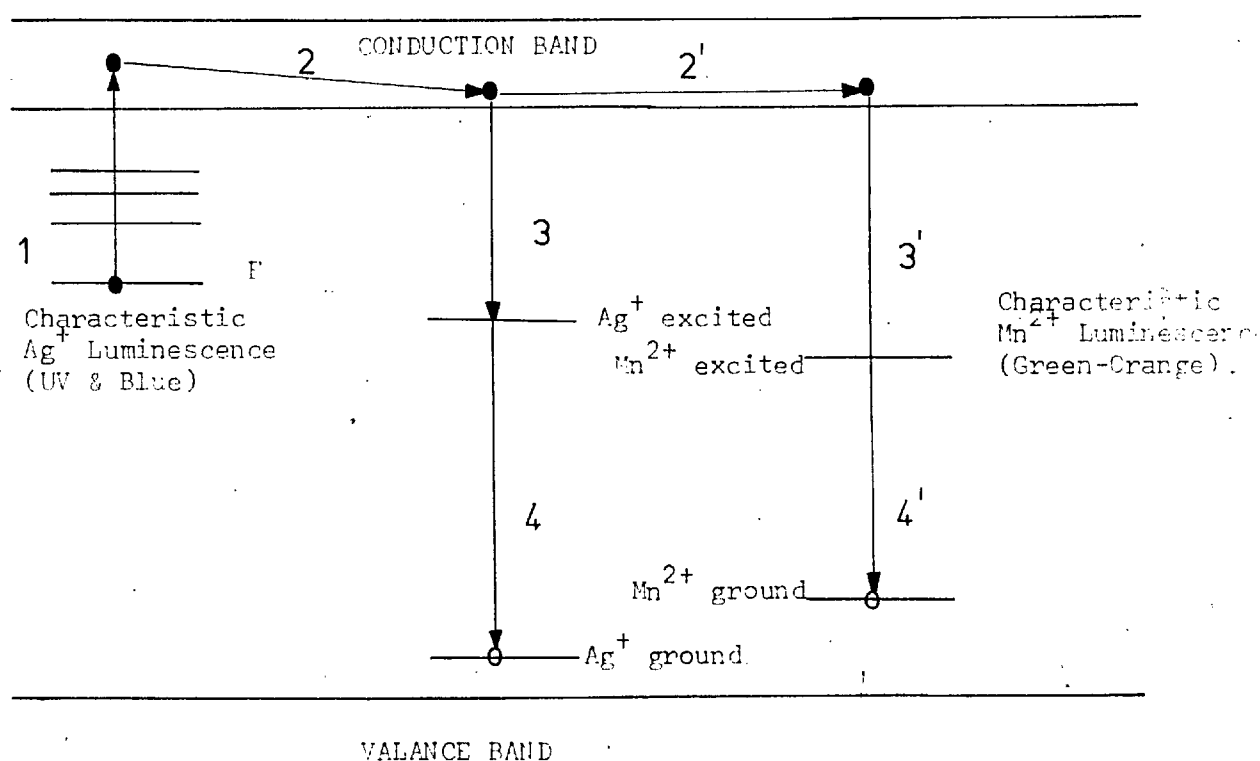
Figure 1.3 shows trapped electron centres (F centres) and trapped hole centres (H or V centres) formed by the irradiation of a pure salt. By absorption of a sufficiently energetic light quantum, or by acquiring the necessary energy from the thermal vibration of its surroundings, an electron may be completely ejected from the F centre into the conduction band (step 1). It can then wander through the crystal (step 2) and recombine with a trapped hole (step 3), giving out the energy of recombination in the form of a light quantum. If the initial step is provoked by light absorption the resultant phenomenon is called 'optically stimulated luminescence'. If provoked by heat, it is known as 'phosphorescence'. When the phosphorescence is accelerated by raising the temperature it is called thermoluminescence. An equivalent series of processes can also take place (1', 2', and 3') wherein a hole is optically or thermally liberated from its trap and migrates via the valence band, light being emitted with recombination of the free hole with a trapped electron.



Thermoluminescent Processes in an Alkali Halide containing Colour Centres.
(and Optically Stimulated Luminescence.)

Fig. 1.3.

● Electron
○ Hole



Thermoluminescent Processes in an Impurity-Activated Alkali-Halide leading to Luminescence Characteristic of the Impurity. (Mn^{2+} & Ag^+ as examples.)

Fig. 1.4.

In order to ensure that stage 3 (or 3') results in radiation of visible wavelength and so that the emission spectrum can be controlled, the system can be doped with known luminescent ions or activators. Figure 1.4 shows how silver (Ag^+) or manganese (Mn^{2+}) can function as activators. On irradiation, the electron trapping leads to F centre formation as before, but the hole is now trapped at a specific site, namely that of the activator ion. On ejection of the electron from the F centre, it recombines with the hole at the Ag^+ or Mn^{2+} ion, thus exciting characteristic activator luminescence, which is ultraviolet-blue in the case of Ag^+ and green-blue for Mn^{2+} .

The concentration of electron and hole traps can also be influenced by doping with impurities. Figure 1.5 shows how a divalent positive ion impurity can exist in the crystal. In order to compensate for the excess positive charge, an alkali ion must be omitted from the structure. Thus, for every substitutional divalent impurity ion added, a positive vacancy is created. Apart from the changes which the impurity ion makes in the relative proportions of positive and negative ion-vacancies, it can also act as a trapping centre, and the complexes formed are sites where radiation-induced changes can take place more easily than at normal lattice sites. These effects will be discussed more fully in Section 2.2. in the context of dosimetry grade lithium fluoride (TLD-LiF) which uses magnesium and titanium as activators.

1.4. Theory of Glow Curves Based on the Band Theory of Solids

Investigations of the phenomenon of thermoluminescence in a given phosphor are concerned mainly with obtaining information on the 'decay curve', *i.e.* the rate of decay of the emitted light when the crystals are kept at a constant temperature; and the 'glow curve', *i.e.* the variation of light emission with increasing temperature (or time if a linear heating rate is applied).

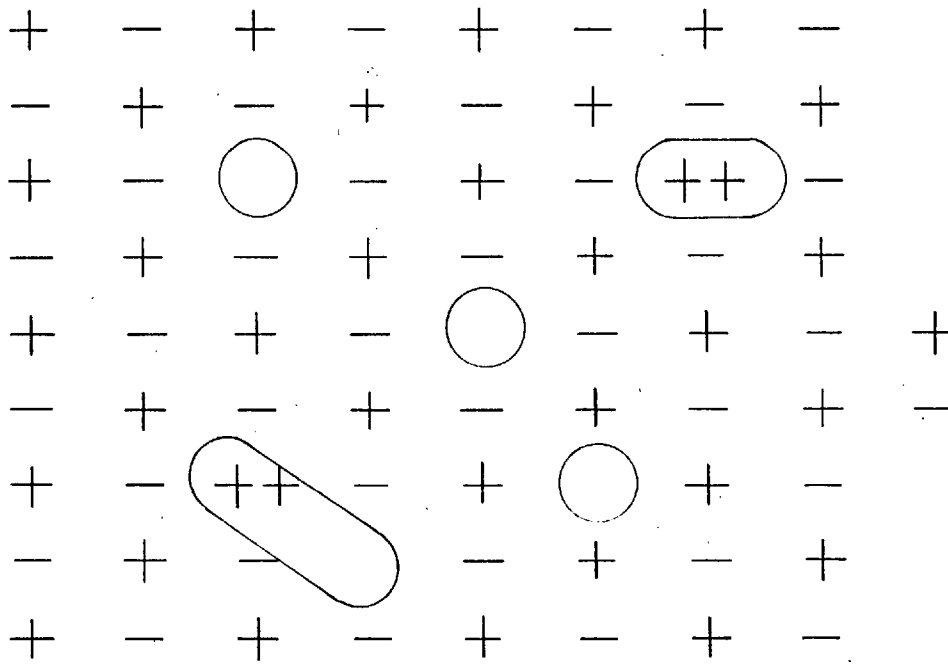


Fig. 1.5. Schematic representation of Vacancies, Substitutional Divalent-Cation Impurity, and Vacancy-Impurity Complexes.

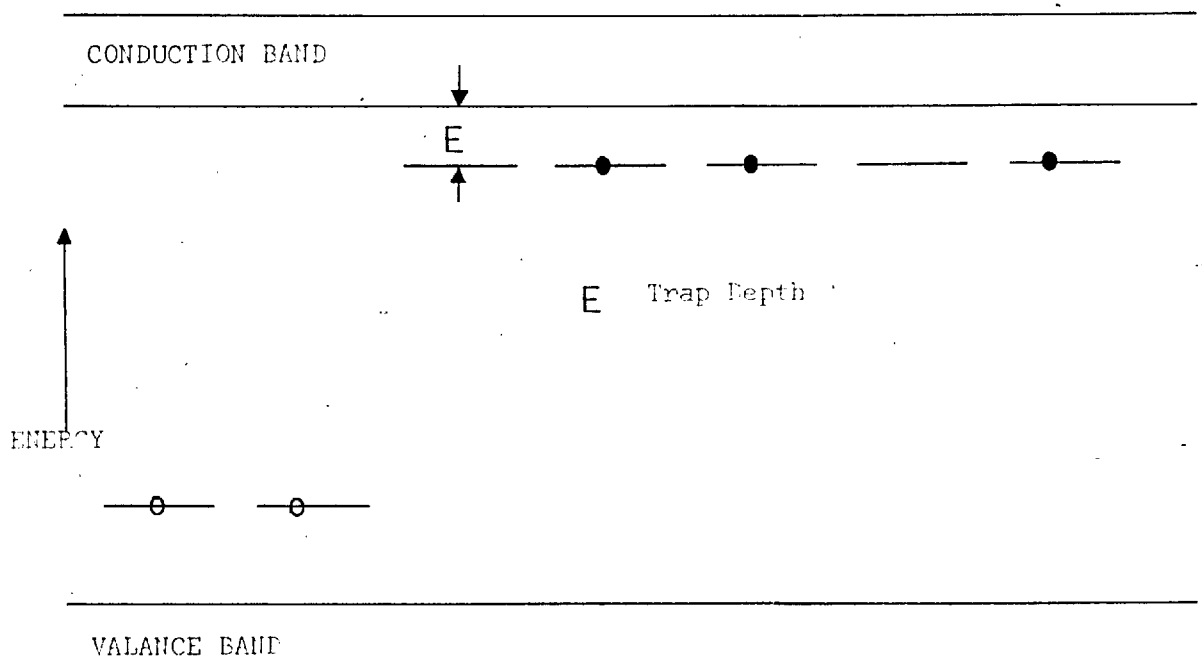


Fig. 1.6. Energy-Level Diagram for Thermoluminescence from Single Type of Trap.

- Electron
- Hole

Urbach (15) suggested a quantitative theory of glow curves based on the band theory of solids, which was developed by Randall and Wilkins (16). This can most easily be explained by considering the case in which only one type of electron trap exists, having a depth E below the conduction band (Fig. 1.6). On heating at a constant rate of β/sec , the freed electron is not retrapped but undergoes recombination with a positive hole, emitting light. The rate-determining process for luminescence is that of the rate of escape of the electron from the trap. If τ is the mean lifetime of an electron in a trap, the probability per unit time of ejection of the electron is given by

$$p = \frac{1}{\tau} = s e^{-E/kT}$$

where T is the absolute temperature

k is the Boltzmann's constant

and s is a factor having dimensions of frequency and related to (although generally much less than) the frequency of atomic vibrations in solids.

The luminescence intensity is determined by the rate of emptying of the traps

$$I = -\frac{dn}{dt} = n_0 p = n_0 s e^{-E/kT}$$

where I is the luminescence intensity

and n_0 is the number of electrons initially trapped.

Since the phosphor is heated at a constant rate, $dT/dt = \beta$

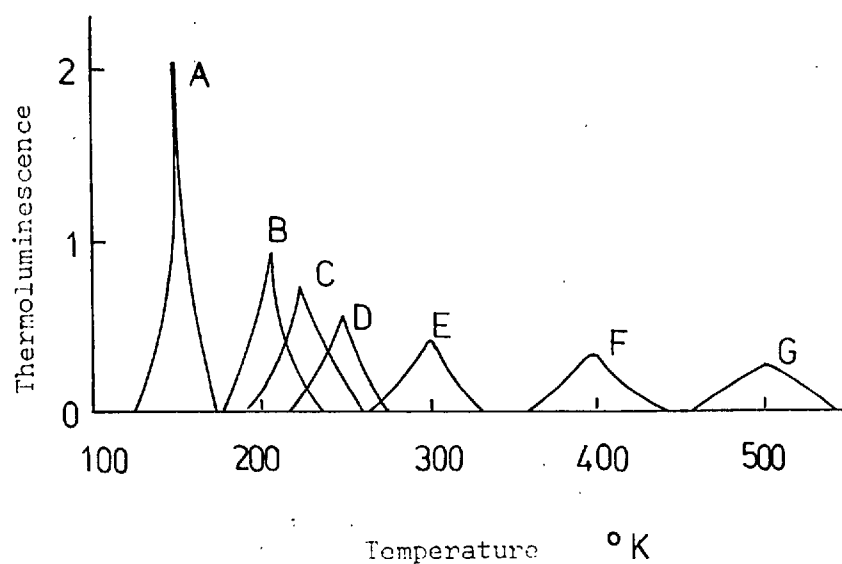
$$-\frac{dn}{dt} = -\beta \frac{dn}{dT} = n s e^{-E/kT}$$

$$\text{whence } n_T = n_0 \exp \int_{T_0}^T -\frac{s}{\beta} \exp \left[-\frac{E}{kT} \right] dT$$

and

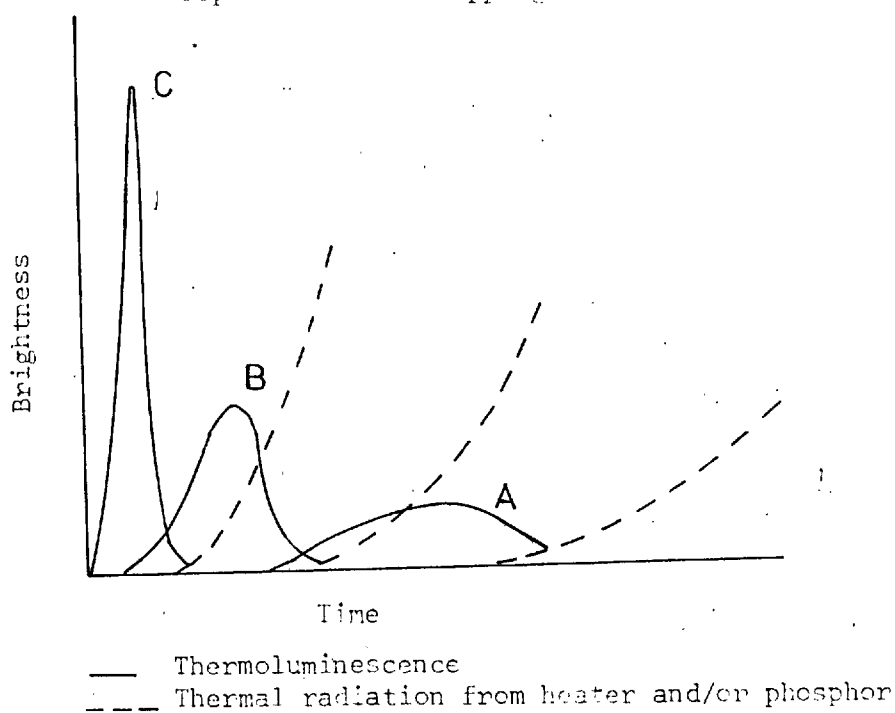
$$I_T = n_0 s \exp \left[-\frac{E}{kT} \right] \exp \int_{T_0}^T -\frac{s}{\beta} \exp \left[-\frac{E}{kT} \right] dT$$

Figure 1.7 shows the graphical representation of this last equation.



	E, eV	s. sec ⁻¹
A	0.3	10^9
B	0.4	10^9
C	0.4	10^8
D	0.4	10^7
E	0.6	10^6
F	0.8	10^9
G	1.0	10^9

Fig. 1.7. Theoretical Glow Curves for Phosphors with Single Trap Depth and No Retrapping.



The luminescence increases as electrons are ejected from the traps by the increasing temperature, reaching a maximum at T^* , and then decreases as the store of electrons is depleted. T^* moves to a higher temperature if E or β increases, or s decreases. The area under the curve is proportional to n_0 . In dosimetric use this is determined by radiation exposure or dose. For a particular type of trap, E and s are fixed; if a fixed arbitrary heating rate is used then the glow peak height can be used as a measurement of n_0 .

If the phosphor contains several different types of traps, each with their own characteristic E and s values, then the glow curve will consist of several different peaks. Those having low E and high s values will not store energy well; e.g. traps having $E \leq 0.8\text{eV}$ along with $s \geq 10^9 \text{ sec}^{-1}$ will suffer severe depopulation in one day or less (mean life ≤ 1 day) at room temperature.

The major problem is to determine the trap parameters from the experimental glow curves obtained. At $T^* \quad \frac{dI}{dT} = 0$ giving $\beta [E/T^{*2}] = se^{-E/kT^*}$ so that E is an implicit function of T^* , defined by the parameter $\theta = \beta/s$. For normal values of β (1°K sec^{-1}) and s (10^9 sec^{-1}) an empirical relation given by Urbach (13) holds approximately,

$$E(\text{in eV}) = T^*/500$$

For higher values of θ , that is faster heating rates or lower s factors, the denominator increases considerably, for example, a trap depth of 1 eV at 100 times faster heating rate ($\theta = 10^{-7}$) would give a peak nearer 600°K rather than 500°K .

The thermoluminescent output can be measured in two ways, either as the integrated light output, known as the light sum, or as the glow peak height. In principle the former measurement has the advantage of being independent of heating rate, so that this rate need not be accurately reproducible between each reading; but it has the disadvantage

that a certain arbitrariness is introduced in deciding the limits of integration, especially in dealing with low doses and hence small signals which overlap the incandescence signal from the heater. The peak height method of measurement requires that the heating schedule be accurately reproducible since peak height is affected by the heating rate (as shown in Fig. 1.8). The glow curves can also be modified by heat treatment of the phosphor, which is discussed in Section 2.2.

1.5. General Properties of Phosphors

By combining the requirements of production of glow curves with that of operational considerations, the factors required in a good thermoluminescent phosphor can be compiled:-

1. A high concentration of electron or hole traps.
2. A high efficiency of luminescence when the electrons (or holes) are thermally released and recombine.
3. Long storage of trapped electrons (or holes) at normal working temperatures, that is large E and low s values.
4. A simple trap distribution, preferably involving a single type of trap to facilitate operation and interpretation.
5. A distribution of luminescence such that it matches the detector, generally a blue-sensitive photomultiplier tube, and which is separated as far as possible from the incandescent emission of the heating source. (Thus, near ultra-violet, blue or green emissions are preferable.)
6. Stability of traps, activators and host lattice to radiation, *i.e.* radiation should fill existing traps without creating new traps or activators and without destroying existing traps or activators.

Further requirements can, of course, be added depending on the intended use for the dosimeter. From the vast list of phosphors known to exhibit thermoluminescence, investigators have tended to concentrate mainly on three systems; calcium fluoride (CaF_2),

calcium sulphate (CaSO_4) and lithium fluoride (LiF). In each case at least one dopant is included in the system; for the first two phosphors this is manganese and for lithium fluoride it is magnesium. The different properties of the crystal make them suitable for different applications. $\text{CaF}_2:\text{Mn}$ has stable high temperature peaks and hence its use is confined to that of health physics as a replacement for film badges. $\text{CaSO}_4:\text{Mn}$, because of its increased sensitivity, is presently being used to detect low intensity radiation, whilst LiF is widely used in routine dosimetry since its effective atomic number for the photo-electric effect closely resembles that of human tissue, 8.14 compared with 7.42 for tissue and 7.64 for air.

1.6. Thermoluminescent Dosimeters

In 1953 Daniels *et al* (9) published an article indicating the possibilities of applying thermoluminescence to the fields of geological stratigraphy, geographical age determinations and radiation dosimetry. It is the last of these that is of importance here. Daniels *et al* showed that the intensity of thermoluminescence is nearly proportional to the amount of γ -radiation received and that of all the crystals tested LiF seemed to have the best response together with the advantage of being stable, insoluble and nondeliquescent. Following on from Daniels proposals, instrumentation was rapidly developed (17,18,19) and exposures of 10-1,000 roentgens could be measured with ease, measurements of less than 1 roentgen requiring slightly more sophisticated equipment.

The first applications of thermoluminescence to dosimetry were made by Daniels' (20) using LiF to measure radiation absorption levels after a series of nuclear bomb tests in the United States of America. Daniels also experimented in the use of LiF for '*in vivo*' dosimetry, allowing a patient who had received a therapeutic dose of radioactive iodine ^{131}I to swallow a single crystal of LiF which was later recovered and analysed.

The major advantage of LiF is that its thermoluminescence is unusually bright and colouration comes in the ultraviolet spectrum, unlike the other alkali halides which absorb yellow or blue light in the visible spectrum and fade-out on continued exposure to daylight. Despite these advantages, work on LiF was abandoned due to the complexity of its behaviour and the practical difficulty encountered in preparing uniformly-doped crystals. Early experimentation had been carried out on single crystals of cross sectional areas approximately 1 cm^2 and weighing 0.3 g, but from one crystal variations of between 50 and 100% were encountered in the sensitivity response to thermoluminescence. In order to try and obtain some sort of uniformity the material was ground, mixed thoroughly and pelletised. These pellets exhibited a new low temperature thermoluminescence after irradiation which decayed with time at room temperature, thus introducing a variable that depended on the number of days of storage between irradiation and read-out. Several attempts were made to reduce this effect, known as triboluminescence, such as the use of optical filters and grinding at different temperatures. It was also found that the sensitivities were affected by the metal casing in which the pellets were put; *e.g.* silver, iron or nichrome. Thus it was decided to look for another crystal to substitute for LiF and research into the use of alumina (Al_2O_3) and $\text{CaSO}_4\text{:Mn}$ began (18,21).

Fused alumina was developed for this purpose, and although it is chemically inert and does not exhibit triboluminescence, its thermoluminescent sensitivity is only about half that of LiF. It is also brittle and the powder cannot be pelletised, but it can be cemented into small silver cups by means of fused silver chloride. Some fairly satisfactory results were obtained using such Al_2O_3 dosimeters (18,22), but the silver chloride tends to darken on exposure to sunlight and the dosimeters must, therefore, be shielded from the light. Research on $\text{CaSO}_4\text{:Mn}$ indicated that the material had too shallow a trap depth to make it a useful substitute.

From the mid-1950's to the early 1960's there was a period of suspended animation in this field of research. With the development of a manganese-activated calcium fluoride phosphor ($\text{CaF}_2:\text{Mn}$) (23) which had high sensitivity and a relatively simple distribution of stable trapping centres, interest rekindled. Utilising this phosphor in an appropriately designed dosimeter configuration (24) the potential of TLD was realised. During this revival the thermoluminescence of LiF was again explored and LiF studies proliferated (25,26).

CHAPTER 2

Thermoluminescence in Lithium Fluoride2.1. Introduction

There are two main spheres of discussion at present in the field of thermoluminescence, namely, what roles do the impurities play in the phenomenon of thermoluminescence, and what are the mechanisms that influence the production of glow curves during different annealing techniques and with differing activator dopant levels? The majority of investigators so far have tended to concentrate on the TLD-100 LiF system, probably because this material is readily available (since it is a commercial product) and is already being used in radiation dosimetry. Consequently, most of the research has been on material obtained from one source, the Harshaw Chemical Company. Only recently has research on specially grown LiF been carried out, at the National Physical Laboratory (NPL) (26, 27, 28), ^{by} Dryden *et al* (29, 30, 31) and ^{by} Stoebe *et al* (32, 33, 34). In these cases the dopant activator level could be properly controlled.

Work at NPL had produced a single crystal of LiF doped with appropriate amounts of magnesium and titanium but which showed no recognisable thermoluminescent response on irradiation (26, 28). On crushing the material into a powdered form, and thus producing a more uniform activator distribution, the thermoluminescent response was found to be good. The present work was initiated after discussions with NPL with the intention of examining more closely this (apparent) phenomenon. On the practical side it was decided to attempt the production of a dosimeter in a compacted form that would be capable of monitoring radiation with the same, or better, degree of sensitivity as the powdered LiF presently being used. Commercial compacted dosimeters are available but these are generally in a Teflon matrix, whereas it was hoped that the dosimeter to be produced in this work should consist only of TLD-LiF.

The technique developed by NPL for growing single crystals of TLD-LiF allows strict control over the impurity additions, permitting research into the effect of differing dopant levels on the thermoluminescent response. It was therefore decided that the present work should include a systematic study of some of the structural factors that influence thermoluminescence in LiF.

The last decade has seen considerable progress in the characterisation of the thermoluminescence behaviour of LiF and its practical use to dosimetry. The work reviewed here deals with the phenomenon at and above room temperature. Cameron with the help of the Harshaw Chemical Company re-opened investigations on LiF which resulted in the manufacture of a commercial grade thermoluminescent phosphor known as LiF (TLD-100). It was found that purified LiF gave a poor thermoluminescent response, but the addition of magnesium increased the sensitivity to measurable amounts (20, 35, 36). However, this magnesium doped LiF did not always give the same luminescent yield due to the fact that additional impurities are also required for high sensitivity to be obtained. The standard LiF (TLD-100) developed by Harshaw contains a major amount of magnesium and minor amounts of other impurities, including aluminium, europium and titanium (37) of which the last of these has been shown to be the most important (38, 28). There seems, however, to be considerable discrepancy between individual investigators as to the exact composition of this material, see table 4.3. Harshaw themselves have a policy of non-divulgence of exact proportions of the impurities but give a wide range of possible dopant levels (37, 39). Since the shape of the glow-curve is not only a function of instrumentation (see section 1.6) but also impurity content (this will be discussed later) and thermal history some form of standardisation must be employed.

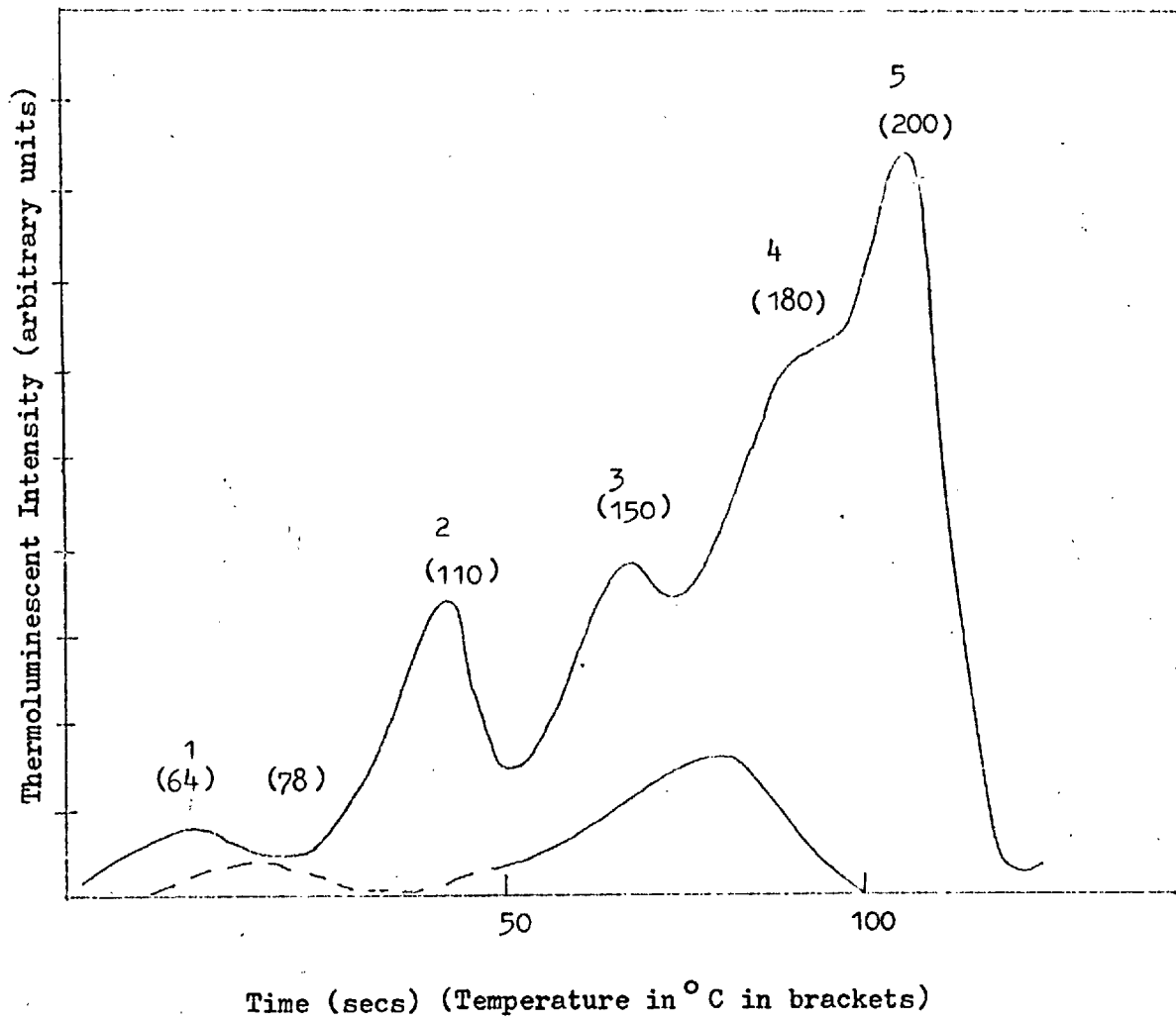


Fig.2.1. LiF TLD-100 Glow Curve.

2.2. Effect of Annealing on the LiF Glow Curves

A typical glow curve for TLD-100 is shown in Figure 2.1. The nomenclature adopted here is that of naming the peaks rather than specific temperatures since peak maxima will depend on heating rate (40). Five major peaks exist which at room temperature decay with the approximate half-lives of 5 minutes, 10 hours, 0.5 years, 7 years and 80 years (41) respectively. Hence it is obvious that for dosimetric considerations peak 1 should be ignored and peaks 4 and 5 concentrated on. It has been discovered (41) that by various combinations of pre- and post-irradiation annealing peaks 1 and 2 can be completely removed and those of 4 and 5 enhanced. In as much as most users of LiF as a dosimetric material follow one procedure a standard pre-irradiation anneal of 1 hour at 400°C followed by 24 hours at 80°C can be adopted. This has the effect of almost eliminating peaks 1 and 2 and considerably lessening the effect of peak 3. The same effect can also be produced by post-irradiation annealing for 10 minutes at 100°C.

Daniels and Rieman (18) observed that the optimum temperature for initial annealing and annealing before re-use was 400°C; this increased the sensitivity by 4 to 5 times. Further studies generally confirmed these findings. Cameron *et al* (35) have produced a comprehensive study of the effects of the pre-irradiation annealing, including the existence of a high temperature peak 6.

The main features of pre-irradiation annealing can be summarised:-

- (i) Heating at low temperatures, 80°C, for a prolonged time tends to destroy the low temperature peak and shift the main dosimetric peak towards high temperatures.
- (ii) Prolonged heating at temperatures between 120°C and 150°C destroys the main dosimetric peak and enhances the lower temperature peaks, the main peak being that of 5.

(iii) After 8 hours at 175°C the main peak is halved whilst the lower temperature peaks are enhanced by a factor of 4 to 5.

(iv) One hour at 600°C reduces the height of all the peaks, whilst 120 hours at 400°C only slightly decreases the main peak and increases the low temperature peaks.

(v) One hour at 400°C causes the main peak to become prominent but also increases slightly the low temperature peak, thus increasing the tendency to fading. If this treatment is followed by 24 hours at 80°C (a procedure accidentally discovered by Buch (35)) the best compromise is obtained, a prominent peak 5 and a very small peak 2.

In most of the present research, as opposed to dosimetry use, a slightly different standard anneal is carried out; that of annealing for 1 hour at 400°C followed by a rapid air quench. Additional pre-irradiation annealing treatments can alter the glow curve in a similar manner (41, 42).

The principal effect of these thermal and also optical treatments, (the latter will be discussed later,) on TLD-LiF is to alter the lattice defect equilibrium (including the concentration and arrangement of cation and anion vacancies, impurities, impurity-vacancy associates and electron-hole pairs which may be associated with such defects). Since the phenomenon of thermoluminescence is thought to be related to the defect equilibrium an understanding of the occurrence, interaction and formation of possible defects is first necessary.

2.3. Defect Equilibrium in LiF

Lithium fluoride, LiF, is a member of the alkali halide group of ionic crystals, see Figure 2.2. The possible intrinsic defects that can exist in such a system have already been dealt with in the preceding chapter. Although high energy radiation may produce Frenkel defects in appreciable quantities (43, 44) the predominant thermal defect is that of Schottky (45). In real crystals there will always be some aliovalent

LiF

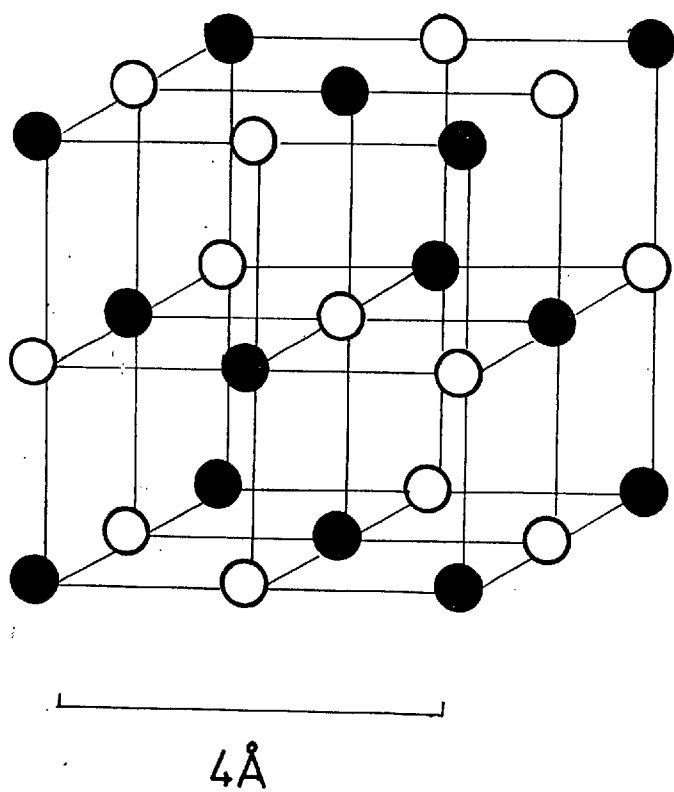


Fig.2.2.

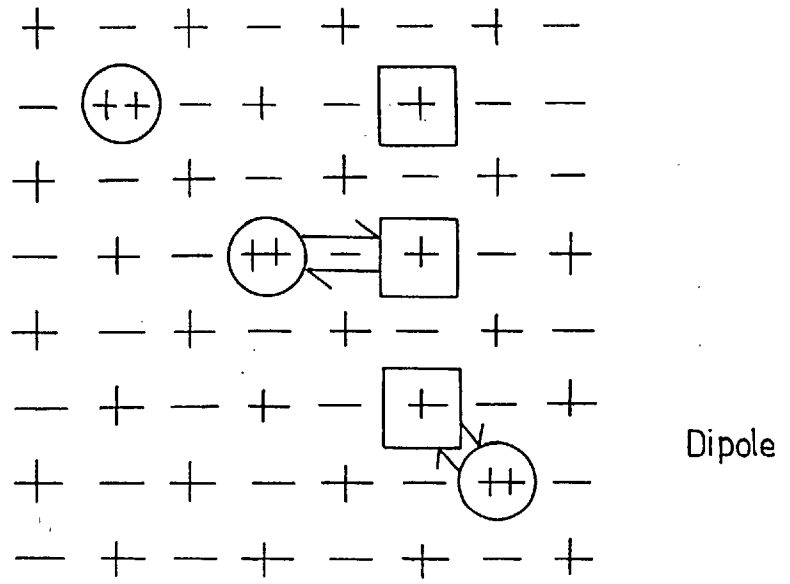


Fig.2.3.

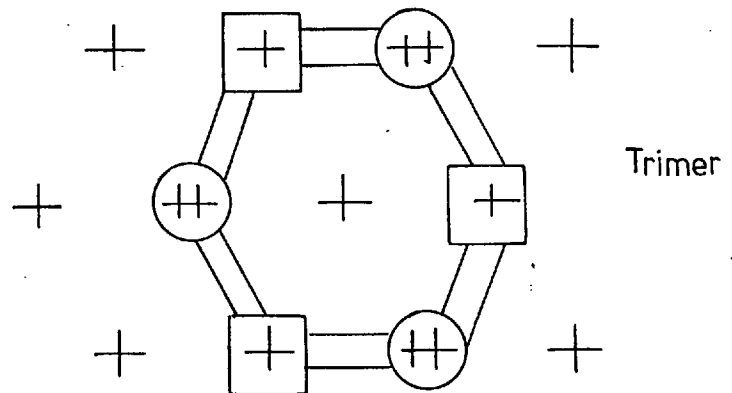
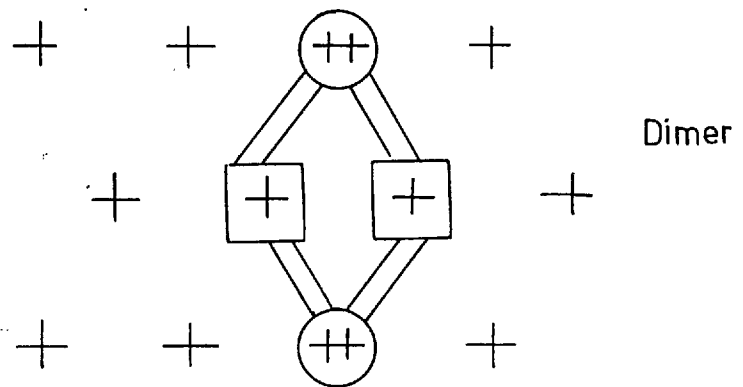


Fig.2.4.

metal ion present, either as background impurity, or intentional doping. In the case of TLD-LiF the main impurity dopant is the divalent Mg^{2+} cation. At low concentrations such impurities reside substitutionally in the cation sublattice. In order to maintain charge neutrality the introduction of a divalent cation necessitates the formation of a compensating cation vacancy, Figure 2.3. Since the divalent ion and the cation vacancy are of unlike charge there will be a coulombic attraction, the net result being that as the temperature decreases there is a tendency for association into pairs (or dipoles) to occur, with a definite binding energy (46, 47, 48).

The existence of higher order complexes was postulated by Haven (49) who failed to account for all the divalent ions known to be present as free ions or associated pairs. Dryden *et al* (50, 51, 52) substantiated and extended this hypothesis for several divalently doped alkali halide systems. They showed that the initial stages of decay of the associated pair concentration with time at various temperatures followed third order kinetics, this was taken to show that three associated pairs were aggregating together to form trimers. They proposed a model, Figure 2.4. comprising of three mutually attracted associated pairs, arranged in a hexagonal 'benzene-type' planar configuration on the (111) plane. They tentatively postulated that the clustering reaction proceeded further by subsequent addition of pairs of dipoles to the trimers to form pentamers, heptamers, *etc.* A consequence of the existence of trimers and possible higher order aggregates is that for a given doping level and temperature there will be a specific concentration of each in solid solution at equilibrium.

Strutt and Lilley (53) have shown that at least in one alkali halide system (Mn doped NaCl) trimers do not form directly from associated pairs but *via* the intermediary of dimers in a two step process

$$D_1 + D_1 = D_2$$

$$D_2 + D_1 = D_3$$

where D_1 indicates a dipole, D_2 a group of two dipoles (a dimer) and D_3 a trimer. Bannaghan (54) has shown that in this system, at low concentrations, quenched-in dipoles do not appear to aggregate further than trimers, but slow cooled specimens do appear to contain higher order aggregates. He also points out that the possible presence of the Suzuki phase in quenched specimens may give rise to the third order kinetics observed.

Other impurities have the potential to change the cation defect equilibrium including trivalent metal ions such as aluminium and also certain divalent anions (55). Of practical importance here is the OH ion which has been shown to form complexes with cation impurity-vacancy dipoles (56) and titanium impurities (33). The anionic defects that are important for their optical activity such as F and V centres have already been dealt with in Chapter 1 and their relation to thermoluminescence discussed.

2.4. Thermoluminescence and Ionic Conductivity

Ionic conductivity measurements offer an excellent opportunity to study the defect equilibrium state since each region in the Arrhenius plot can be related to a specific defect present in thermal equilibrium. The theory relating such measurements has been well documented (57) and several reviews are available (58, 59, 60); a brief resume only of the relevant theory will be discussed here.

Figure 2.5. shows a schematic conductivity temperature plot, the regions are designated according to the notation of Dreyfus and Norwick (61).

Ionic conductivity σ , can be expressed by the simple relationship

$$\sigma = ne\mu \quad (1)$$

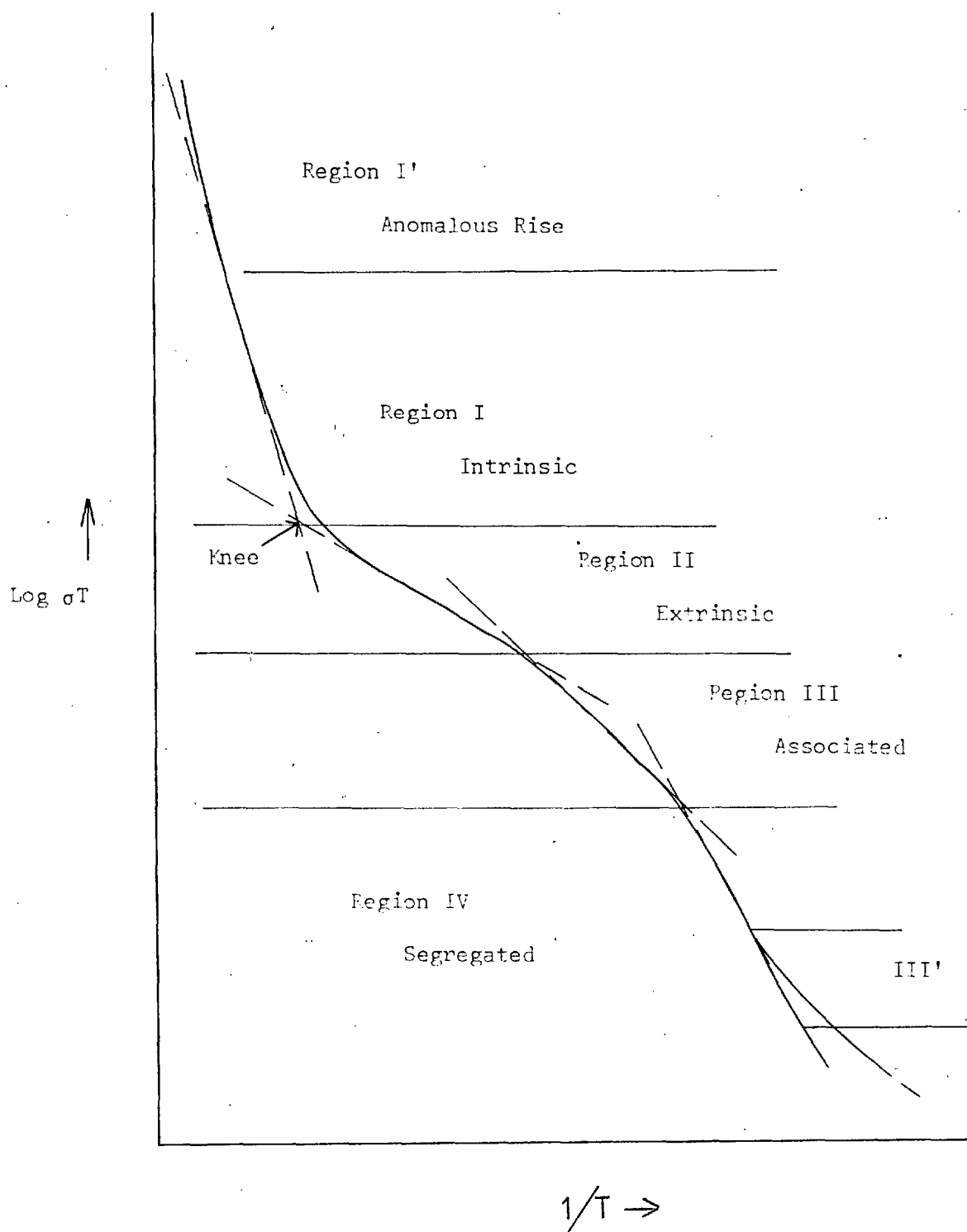


Fig. 2.5. Schematic Conductivity-Temperature Plot.

where n is the vacancy concentration, e the charge and μ the mobility.

In a pure crystal the number of vacancy pairs (Schottky defects) present can be calculated by applying the thermodynamic equilibrium condition of free energy.

$$\frac{n}{N} \propto e^{-Q/2kT} \quad (2)$$

where N is the number of ions, Q the energy of formation, k Boltzmann's factor and T the absolute temperature. In order for conduction to take place the vacancy must move, this depends on the probability, p , of the vacancy having the correct activation energy E to jump to the new site

$$p \propto e^{-E/kT} \quad (3)$$

The rate of diffusion, D , though depends on the density of the vacancies and the jump probability

$$D \propto n/N \quad (4)$$

Equating 2 and 3

$$D \propto e^{-(Q/2 + E)/kT} \quad (5)$$

Einstein related the conductivity to diffusion by the equation

$$\frac{\sigma}{D} = \frac{Ne^2}{kT} \quad (6)$$

and since

$$D = D_0 e^{-(Q/2 + E)/kT} \quad D_0 \text{ being a constant}$$

$$\rightarrow \sigma kT = D_0 Ne^2 e^{-(Q/2 + E)/kT} \quad (7)$$

$$\text{or} \quad \log(\sigma T) = \text{constant} - 1/kT(Q/2 + E) \quad (8)$$

Hence a plot of $\log(\sigma T)$ against $1/kT$ should yield a straight line of slope $(Q/2 + E)$ which is characteristic of the intrinsic region. This is the region known as I.

Region II is that related to the extrinsic defects, the dopant participation. In this region the divalent ions and cation vacancies are considered to be unassociated. The conditions of electrical neutrality are substantially altered. There is an effective positive charge equal to e times the number of divalent cations present. The number of

intrinsic defects (cation and anion vacancies) present will decrease to zero as the temperature falls, the number of Li^+ vacancies however, remain constant and equal the number of Mg^{2+} ions. This condition can be applied by equating Q to zero in equation 8.

$$\log (\sigma T) = \text{constant} - 1/kT(t)$$

Hence the slope of region II will give a value for the activation energy of the dopant ions. The point of transition from extrinsic to intrinsic region is known as the knee temperature; depending on the level of doping the knee temperature will alter although the slope remains constant.

In region III aggregation of the free divalent ions and vacancies occur to form associated pairs, trimers and possibly higher order complexes. As a result of this association the number of free vacancies available for conduction decreases, the slope of the conductivity plot is given by $\log(\sigma T) = \text{constant} - 1/kT(E - h_k/2)$ where h_k is the energy of formation of the associated species.

Region IV is correlated to the formation of precipitates; the divalent ions and cation vacancies disappear the net result being a further increase in the conductivity curve.

In applying ionic conductivity measurements to the phenomenon of thermoluminescence much information can be gleaned. Vora *et al* (32) have carried out a systematic investigation into the influence of lattice defects, comparing the conductivities of various known dopant-levels of LiF to that of TLD-100. Figure 2.6. Their results indicate that for TLD-100 between 250°C and 450°C dipoles are the predominant defect, and the occurrence in region IV of a metastable $\text{MgF}_2 \cdot 6\text{LiF}$ phase, between 150°C and 250°C, while further dipole formation occurs at still lower temperatures. Lilley (62) had previously studied the LiF:Mg system and been able to identify a metastable phase of stoichiometry $6\text{LiF} \cdot \text{MgF}_2$

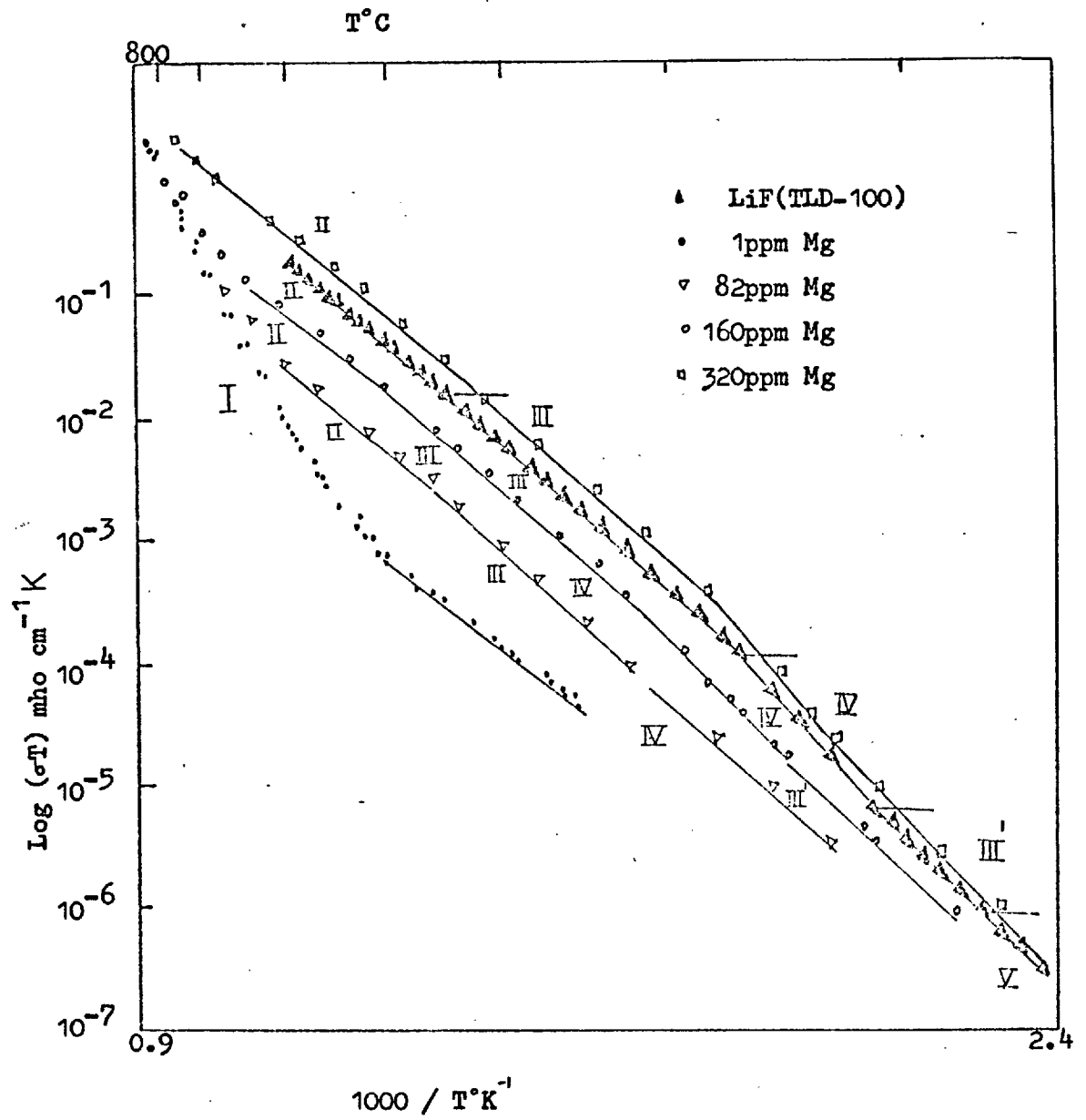
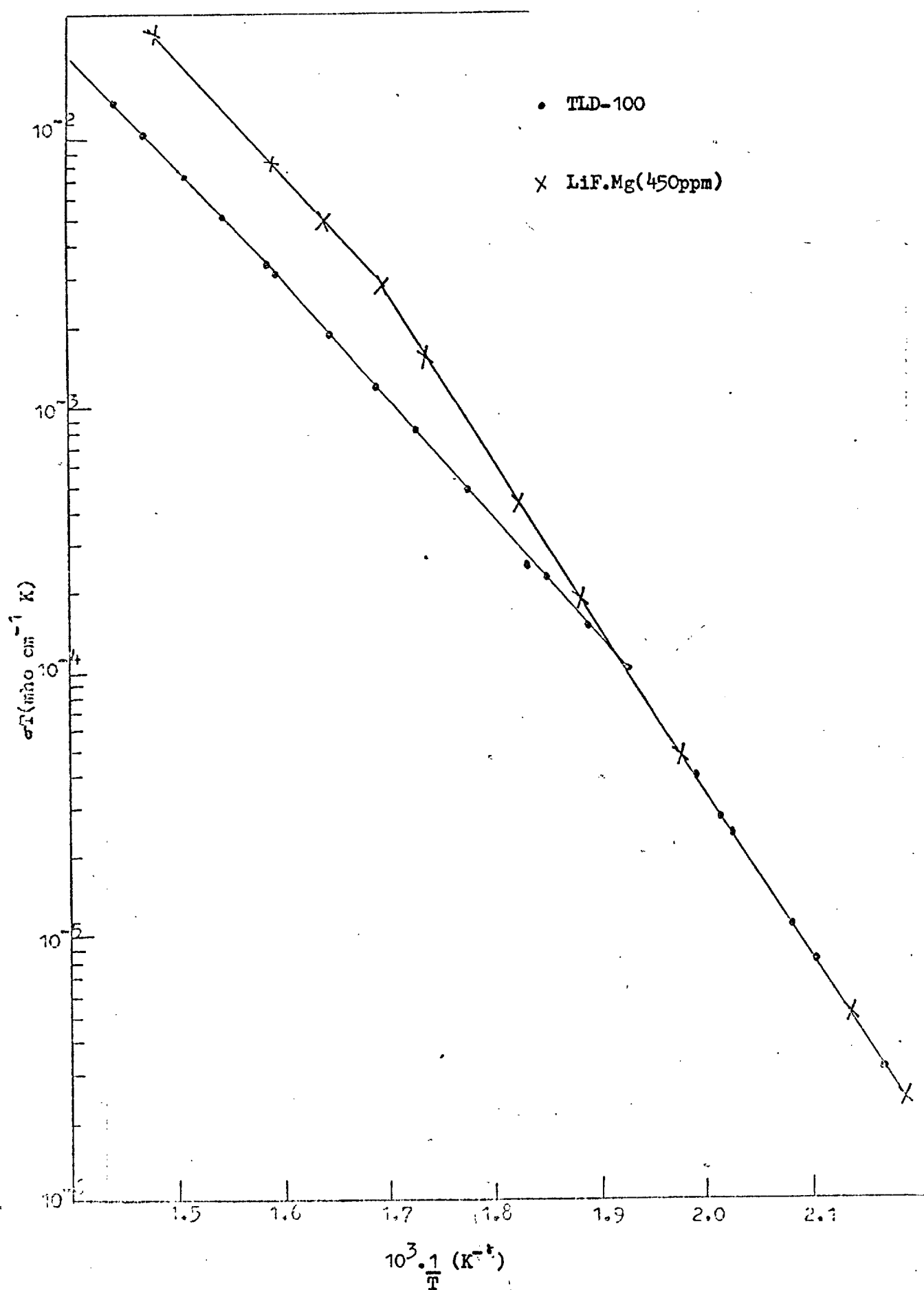


Fig.2.6. Ionic Conductivity Plots.

(Vora, Jones & Stoebe (32))

Fig.2.7. Comparison of Ionic Conductivity Plots for TLD-100 and LiF.Mg(450ppm). (Bradbury(64)).



analogous to the Suzuki phase (63) found in NaCl. Bradbury (64) repeated these experiments on a 450 ppm Mg doped LiF and also on thermally treated TLD-100; the conductivity plots he obtained showed that at low temperatures, that is in region IV, the curves of the two materials coincide, see Figure 2.7. He deduced that since precipitation is known to occur in the doped crystal, TLD-100 must also contain the Suzuki-type precipitate 6LiF:MgF_2 having a solvus temperature of 230°C .

Besides the major impurity of Mg, titanium is known to be an important minor impurity. Ionic conductivity work by Jain and Sootha (65) show that titanium ions behave like other cationic impurities and give a normal plot, indicating that the titanium is present in either a divalent state or in a trivalent form with a compensating cation vacancy, the relevance of this will be discussed later in the role of the recombination centre.

The existence of dimers is indicated by the fact that in the LiF:Mg system a definite III' region is observed (66). This region is correlated to the formation of further dipoles after the Suzuki phase can no longer form due to the low temperature. Dipole formation and equilibrium can more easily be studied using techniques such as ionic thermocurrents (ITC) and dielectric loss (67).

2.5. Thermoluminescence and Dielectric Loss

The possibility that one or more of the thermoluminescent glow peaks can be correlated with the impurity-vacancy complex has been proposed by many authors (68, 36, 31, 69). As yet there is no technique to measure directly the concentration of dimers or higher order complexes; dielectric measurements can only give inferred information. Lidiard (70) gives a detailed analysis. The basic technique is to make use of the fact that the impurity-vacancy pair acts as an electrical dipole in the crystal lattice, by monitoring the dipole concentration by dielectric loss as a function of time after rapid quenching from a suitable temperature at a

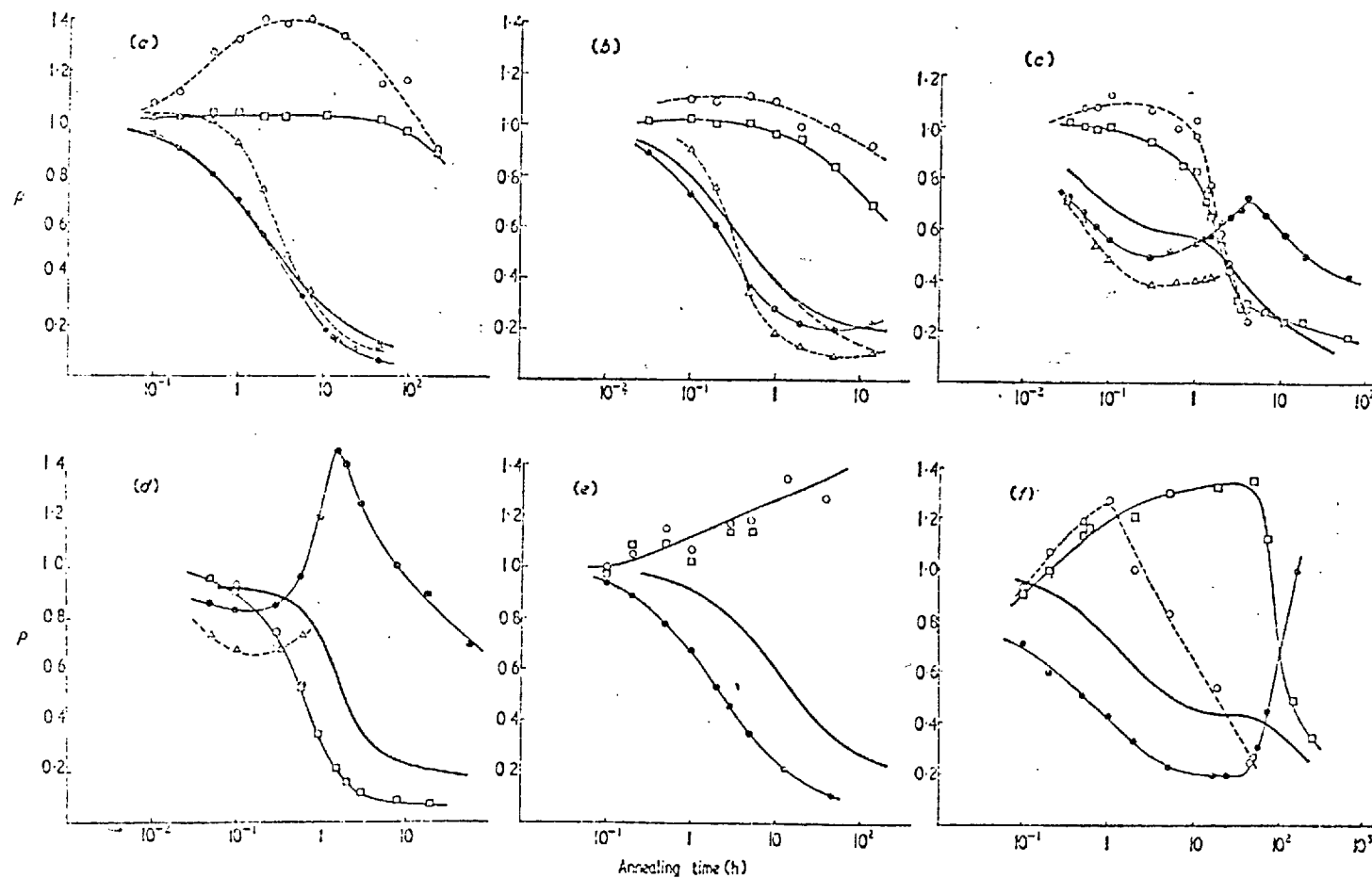


Fig.2.8. The intensity of the dielectric absorption (heavy curves) and heights of peaks 2($\bullet$), 3(Δ), 4($\circ$), and 5($\square$) in *a-d* TLD-100, and *e-f* NSL crystals with 4.4×10^{-5} mol fraction Mg^{2+} , as a function of pre-irradiation annealing time at different annealing temperatures: 70°C; 100°C; 129°C; 150°C; 70°C; 101°C. All measurements are plotted relative to the measurement at $t=0$; that is, immediately after a quench from 400°C.

(Dryden & Shuter (31))

series of constant ageing temperatures it is possible to construct ageing curves, and from these curves deduce the defect clustering models, Figure 2.8.

Grant and Cameron (71) first showed the relation between the concentration of Mg impurity-cation vacancy and peak 2. They performed parallel thermoluminescent and dielectric loss measurements on LiF doped with 70 and 100 ppm Mg at temperatures of 67°C and 95°C, observing a close correlation between the decay in the concentration of associated pairs and decay of the thermoluminescent peak 2; they thus inferred that the same type aggregation was responsible for both phenomena and suggested the Mg^{2+} cation vacancy complex (capturing an electron) since the area of the glow curve was proportional to the concentration of these complexes as measured by loss techniques. Jackson and Harris (72) using this idea showed that the intensity of peak 2 could give a direct measurement of the concentration of dipoles present and suggested that the magnesium-cation-vacancy dipole was responsible for two glow peaks, not one as previously supposed. Comparison of the isothermal decay curves for peaks 2 and 3, and 4 and 5 show that the two higher peaks decay in a similar manner and the two lower, (Figure 2.9), those of peak 2 and 3 exhibiting second order kinetics. Work carried out (73) on the two main absorption bands in TLD-100 showed that each consisted of two components, thus giving good agreement to this idea.

Dryden (30) strongly criticised this work although he later (31) assigned pairs of peaks to similar trapping centres. With Shuter (31) he endeavoured to confirm the relation between the Mg^{2+} cation-vacancy dipole concentration and the intensity of peak 2 at ageing temperatures between 70°C and 175°C and at the same time to ascertain whether any other features of the complex behaviour of the thermoluminescent glow curves could be correlated with particular states of aggregation of the Mg^{2+} ions and their associated vacancies. The closest correlation was found

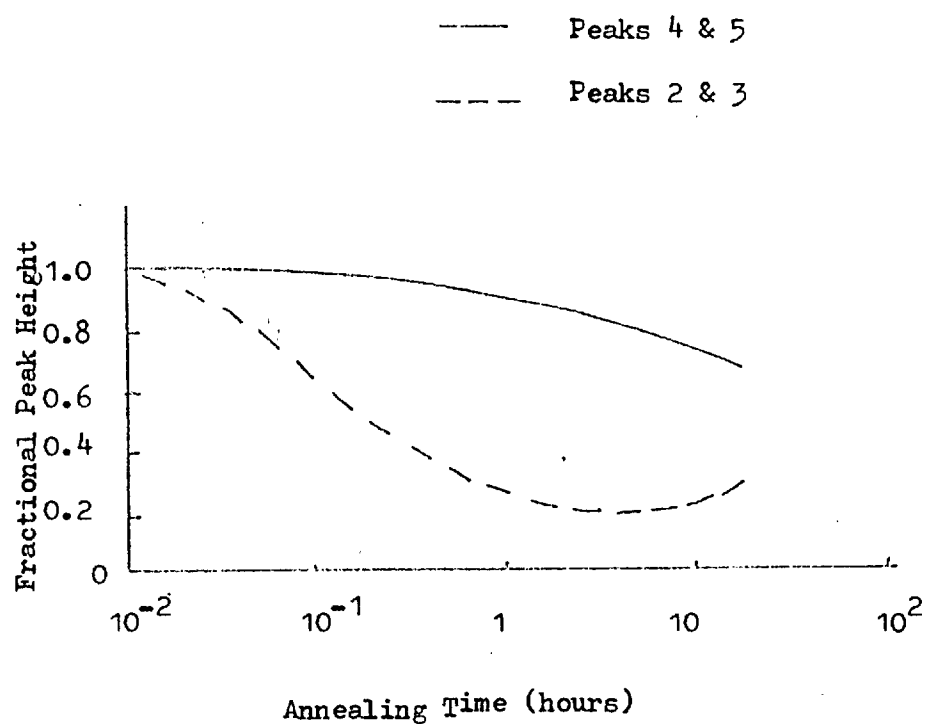


Fig.2.9. Comparison of Isothermal Decay Curves for Peaks 2&3 (---) & 4&5 (—).

to exist at 70°C, the temperature at which Grant and Cameron (71) had performed their ageing; at other temperatures the peak 2 height increased whilst dipole concentration decreased. This invalidated the assumption of Jackson and Harris (72) that the concentration of dipoles can always be measured by the intensity of peak 2. They also showed that one of the factors determining the heights of peak 2 and 3 is the concentration of dipoles in the crystal at the time of irradiation. Those Mg^{2+} vacancy pairs present as trimers and larger aggregates make no contribution to the height of these peaks, both dipoles and trimers contribute to the traps responsible for peaks 4 and 5 but aggregates containing more than three Mg^{2+} vacancy pairs do not contribute and there is competition between traps for electrons (or holes) released by irradiation. Bradbury (64) points out that in neither case was the possibility that the ageing temperature had been suitable for precipitation to occur been taken into account.

2.6. Thermoluminescence and Optical Absorption

Optical studies are of assistance in further determining the identities of specific traps. Most examinations of optical absorption and thermoluminescent properties use essentially the same technique, that is measuring the effects of such parameters as Mg^{2+} concentration, heat treatment and bleaching with light of different frequencies on the optical absorption spectrum, then seeking corresponding changes and hence correlation with the thermoluminescent glow curve.

Irradiation of TLD-LiF produces absorption bands at 380, 310 and 225 nm in addition to the F absorption band at 250 nm (Figure 2.10) (76, 75, 69). The 380 nm band has been correlated with peak 2 (36, 69, 76, 73). That of the 310 with peak 5 (76, 73, 69).

From observations that both the optical absorption band and corresponding glow peak were affected in a similar manner by either pre-irradiation, bleaching or post-irradiation Claffey (68) and Klick (69) concluded that

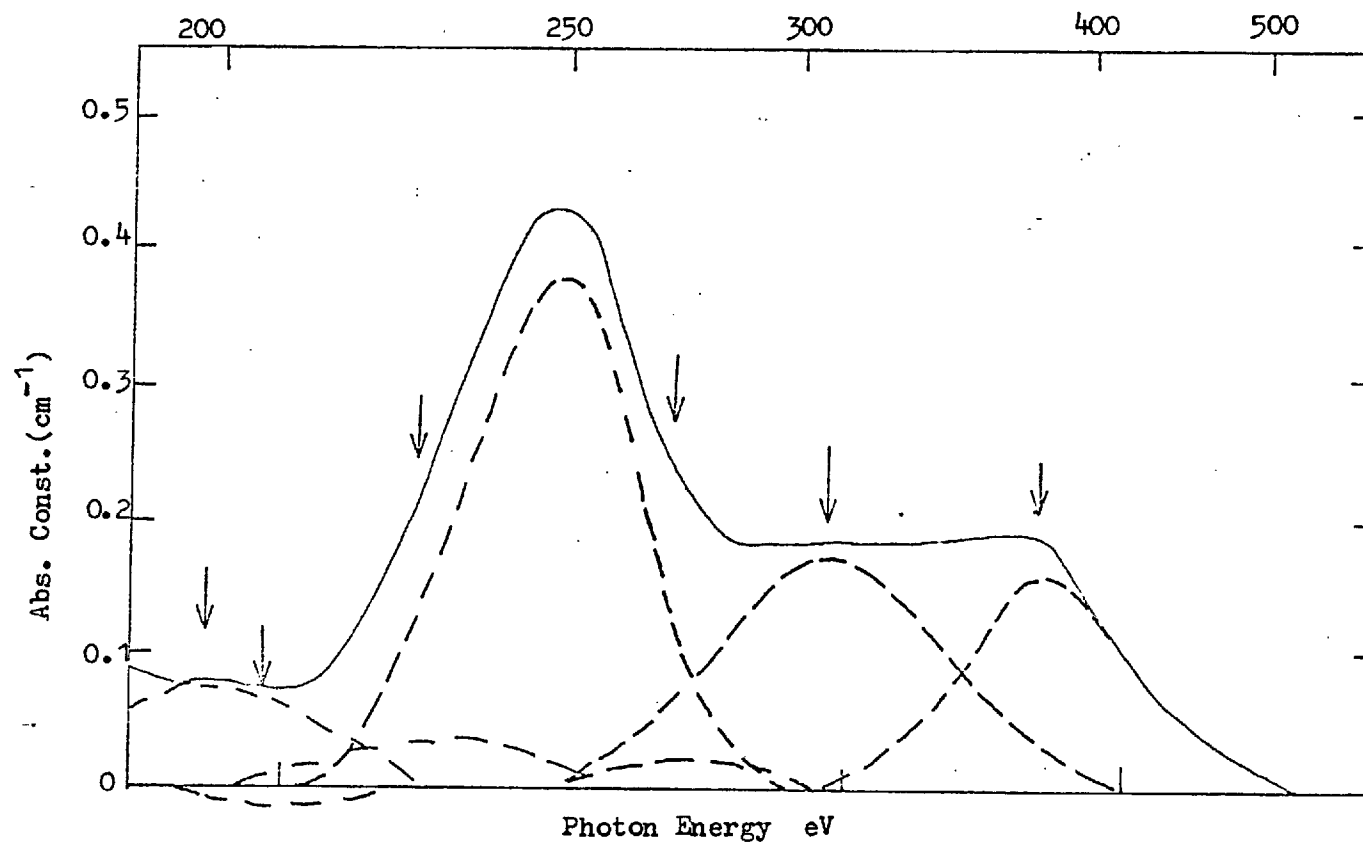


Fig.2.10. Optical Absorption of LiF after Irradiation.

(Mayhugh, Christy & Johnson (77))

the 310 and 380 nm bands were due to trapped hole centres since optical bleaching into the F band destroyed the thermoluminescence and the absorption bands. Christy *et al* (76) found similar results but also observed an absorption band at 196 nm, even in unirradiated crystals. This band was found in TLD-LiF but not in pure LiF. In 1967 Claffey extended earlier work and concluded that this band was not primarily responsible for thermoluminescence, nor could it be correlated with Mg^{2+} content or peak 5. They made four assumptions to explain the centres causing thermoluminescence: (1) that the process begins with thermal release of electrons from trapping centres causing optical absorption at 310 and 380 nm; (2) the centres causing peak IV and V have two excited states so they produce bands at 250 nm as well as at 310 nm; (3) rapid bleaching 310 nm and peak 5 result from one kind of centre and slow bleaching and peak 4 from a different centre; and (4) that the number of luminescent sites is limited.

Although in agreement with Claffey and Christy over the sign of the trapped charge carriers, that is holes, and correlation of bands with peaks Klick *et al* (69) proposed that emission arises from re-combination of a hole thermally excited from the Mg-vacancy complex with the electron at the F centre.

Jackson and Harris (73) considered that if Christy *et al* were correct then isothermal fading of the 310 and 380 nm bands should possess the same characteristics as the glow curves. They showed that both bands decay by a two step process, fast and slow and concluded that each band could be correlated with two peaks as previously discussed in section 2.

Mayhugh *et al* (77) extended the work of Christy to optical measurements in vacuum and ultra-violet; their results combine those of Christy *et al* (76) and Jackson and Harris (72) with two other observations. The trapped charge carrier in the 310 nm defect centre is the electron and the existence of a V_3 centre containing 2 trapped holes absorbing

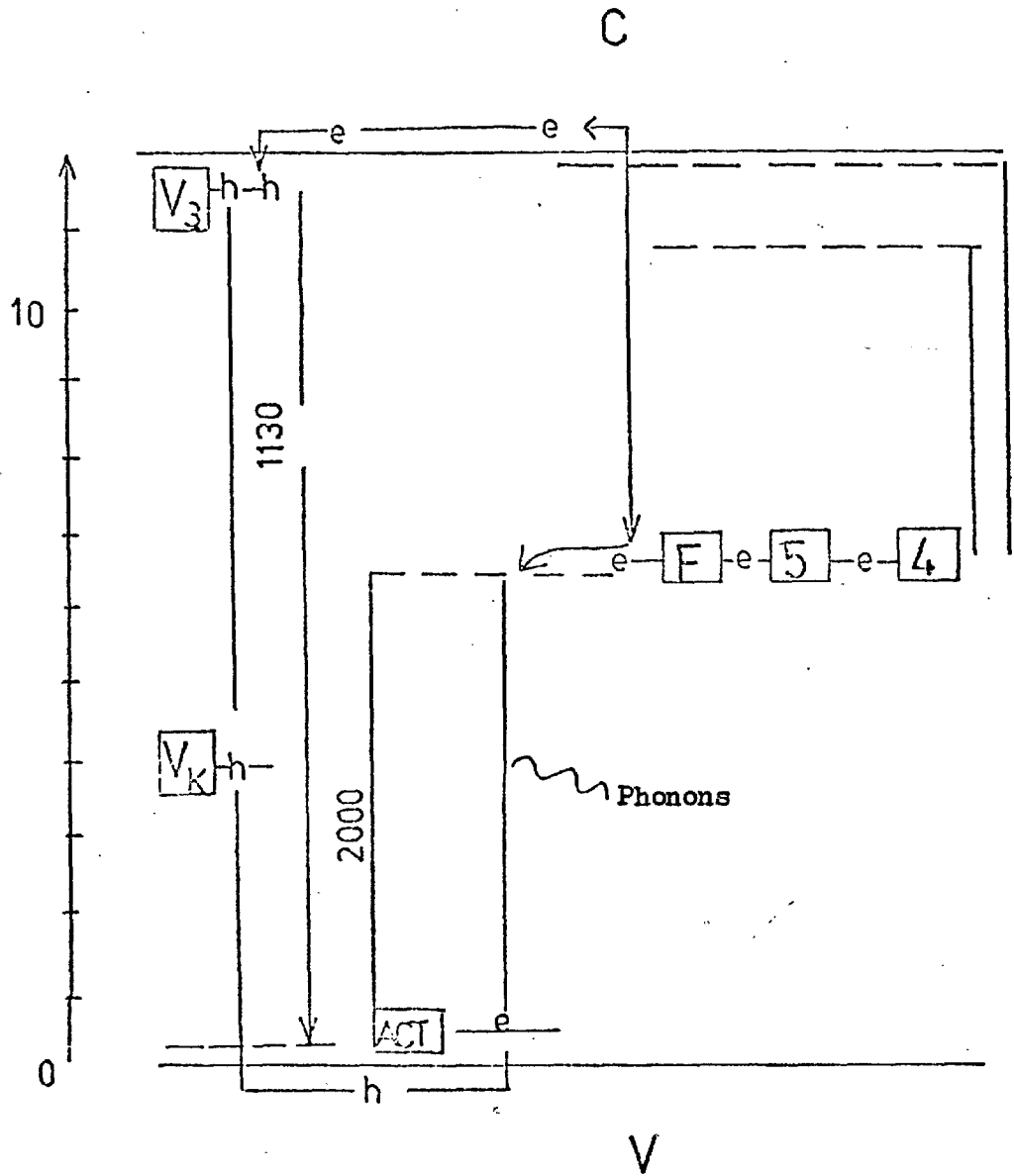


Fig.2.11. Band Gap Model for Thermoluminescence.

(Christy, Johnson and Wilbarg (76))

near 110nm which is intimately involved in the thermoluminescent process. They postulated a band gap model for the phenomenon of thermoluminescence (78), Figure 2.11.

2.7. Thermoluminescence and Recombination

Rossiter *et al* (28, 26) have investigated the relative importance and role of the secondary impurities in TLD-LiF, notably that of the titanium concentration. Examinations of crystals previously grown by them, containing varying amounts of magnesium but no titanium showed a very non-uniform distribution of thermoluminescence along the length of the crystal, although the magnesium distribution was almost uniform (Figure 2.12). Since similar results regarding thermoluminescent behaviour had been reported by Cameron *et al* (25) it was decided to look more closely at the effect of the titanium. The addition of aluminium as Li_3AlF_6 or europium as EuF_3 showed no increase in the sensitivity of the material even though these impurities are stated in the patent specification (37), nor was the distribution of thermoluminescence sensitivity affected. This is in direct conflict with the results reported by Jones and Burt (79) who observed enhancement of thermoluminescent properties of LiF:Mg containing europium. The effect of titanium additives though were to enhance sensitivity (28). A series of crystals of LiF:Mg containing varying amounts of titanium were grown by a technique previously developed (26); these were then sectioned as shown (Figure 2.13) the top 0.8 cm being discarded, the remaining discs and tip were crushed and sieved to investigate the thermoluminescent characteristics, the material left after sieving being used for determination of titanium content by X-ray fluorescence analysis. These results showed that a concentration gradient did exist within each crystal, the highest level being near the tip. Pfann (80) derived an expression to describe the impurity distribution within the crystal as

$$c_x = kc_o(1 - x/L)^{k-1}$$

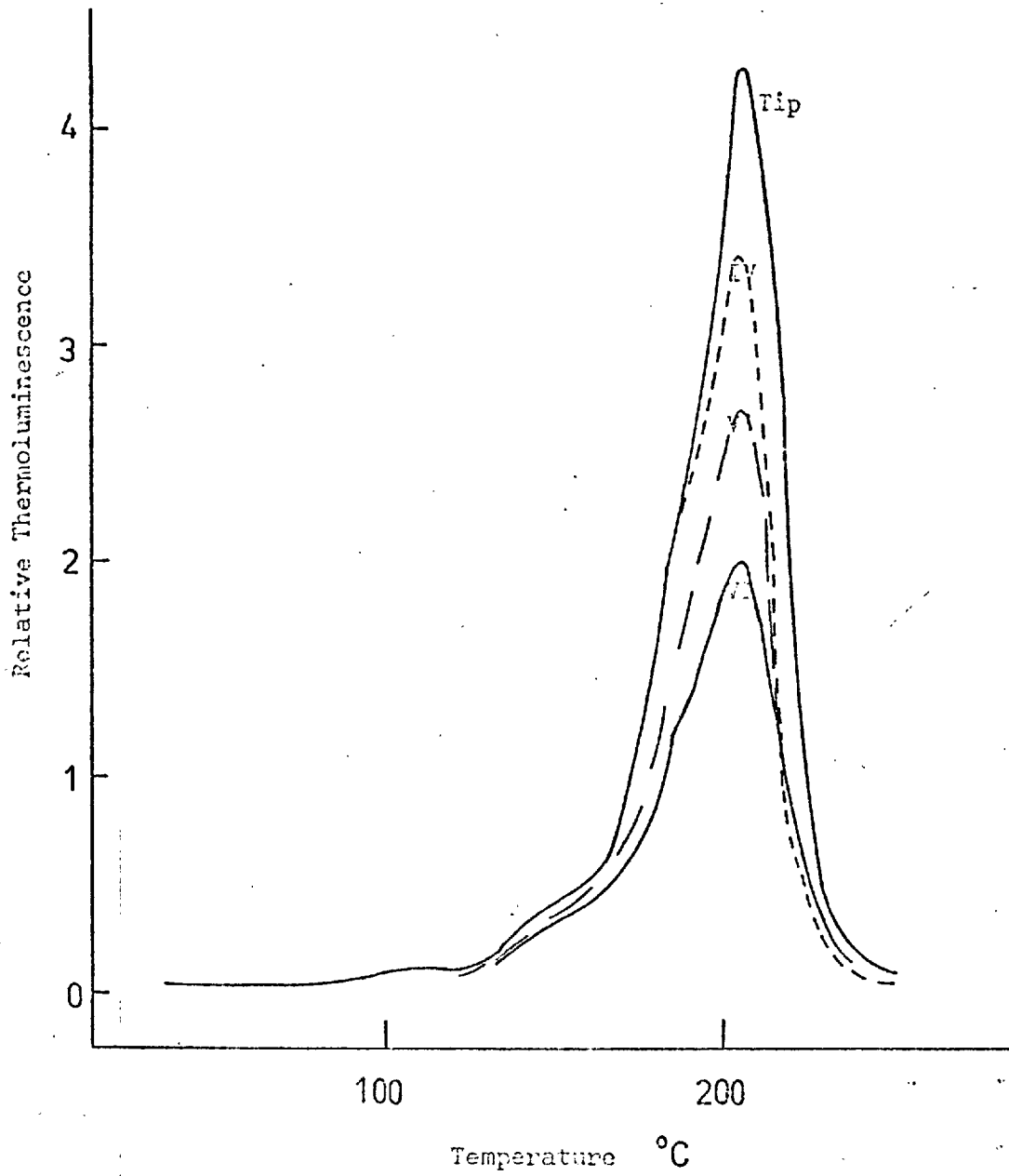
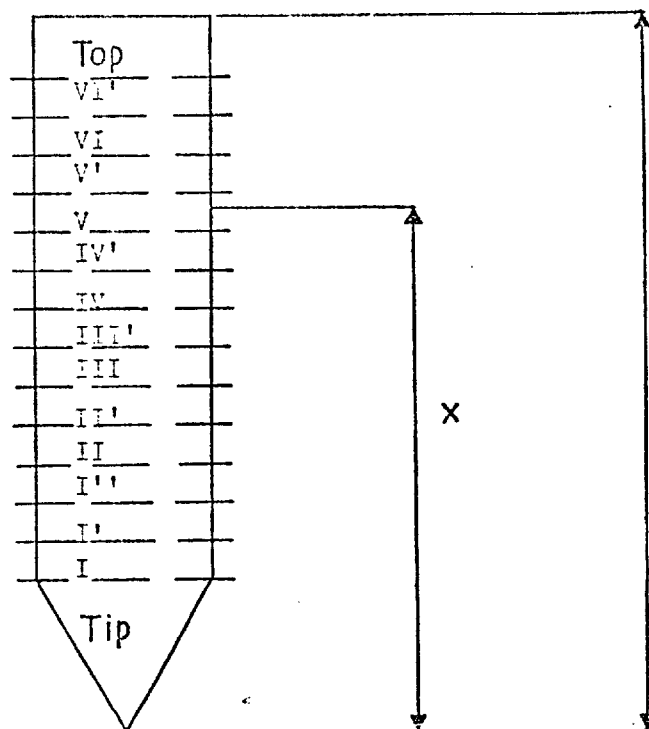


Fig.2.12. Glow Curves obtained from sections of one crystal.



$$C_x = k C_0 \left[1 - \frac{x}{L} \right]^{k-1}$$

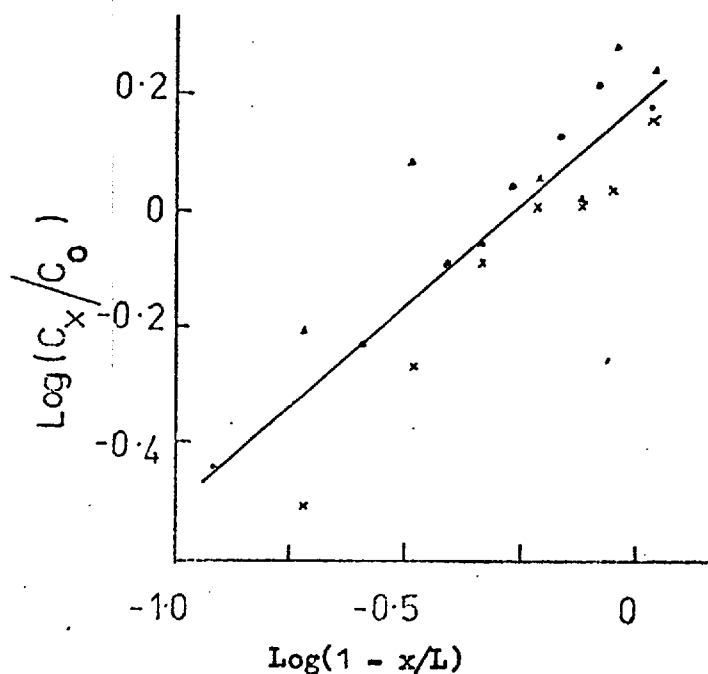
L (8.6 cms)

C_0 - Average Concentration of Impurity in Crystal

C_x - Concentration x cms from Tip

k - Distribution Coefficient of the Impurity

Fig.2.13. Sectioning of Crystal.



Distribution of Ti within 3 Crystals. (•, Δ, ×)

Best straight line yields

$$k = 1.7 \pm 0.1$$

Fig.2.14. Titanium Distribution within Crystal.

where c_x is the impurity concentration at a distance x from a crystal tip, L is the total length of the crystal, c_0 is the average added impurity level and k is the distribution coefficient of the impurity between solid and liquid phases. This may be evaluated by plotting $\lg (c_x/c_0)$ against $\lg (1-x/L)$. A value of 1.7 ± 0.1 was obtained. On examination it was found that a thermoluminescent sensitivity gradient existed that parallels that of the ion concentration. As the titanium content increases however, the distribution sensitivity becomes more uniform until at higher levels (10 ppm titanium) a reverse distribution is found (Figure 2.14), the maximum sensitivity being at around 8 ppm. (The measurement of thermoluminescent output was taken as the area under the glow curve integrated between 175°C and 225°C , peaks 4 and 5.)

Johnson and Williams (36) derived a theoretical expression relating luminescent efficiency, η to concentration of activator; this requires that η rises with activator concentration reaches a maximum and falls owing to luminescence quenching. The variation of relative thermoluminescent efficiency with titanium content obtained by Rossiter *et al* (28) has the same form as that given by Johnson and Williams, indicating the existence of concentration quenching. From the results a parameter Z could be found; this is defined as the number of lattice sites surrounding an activator such that, if anyone of them is occupied by another activator luminescence is quenched. Although a value of Z for the LiF:Mg:Ti system is unobtainable, since an absolute value of the efficiency of the photon emission process is unavailable the low optimum level of titanium points to a high value of Z and a photon emission mechanism involving transitions through the conduction band. Christy *et al* (76) have estimated an efficiency of approximately 1% for the conversion of trapped electrons into photons.

Zimmerman and Jones (38) have shown that the excitation spectrum for photoluminescence of titanium doped LiF is identical with the 200 nm

absorption spectrum and that the photoluminescence spectrum at 200°C was similar to the thermoluminescence spectrum at that temperature. They concluded that the centre responsible for the 200 nm absorption was also involved in the emission of luminescence during the thermoluminescence process. Rossiter *et al* (28) have shown that the 200 nm band is directly related to the titanium content and the luminescent output, indicating that titanium is involved in the luminescent recombination process. Christy *et al* (76) had recognised the 200 nm band as a recombination centre (see previous section) but had not related it to titanium. The apparent titanium content quenching phenomenon would seem to add strong support to the proposals of Mayhugh (78), that titanium acts as a photon emission centre. From work based on absorption studies he proposed the band gap model previously discussed, in which electron-hole recombination occurs at the activator responsible for the 200 nm absorption.

Recent work (32, 33) has shown that hydroxide ion complexes may be involved in the luminescent recombination process. Hydroxyl impurities have been shown to influence the thermoluminescent behaviour of LiF (34) and the 200 nm band has been related directly to the OH ion concentration, leading to the conclusion that OH ions are involved in the recombination process (33). In crystals containing very low OH impurity concentrations the sensitivity was found to be reversed, that is highest sensitivity was observed in the last part of the crystal to solidify; this would mean a distribution coefficient of <1 . This can be explained by the observation that OH ions are rejected from the crystal during growth and only enter the lattice in the last parts of solidification. Stoebe *et al* (33) explain this apparent anomalous behaviour of the 200 nm band by assuming that the band is due to complexes involving two impurities, one with a distribution coefficient greater than 1, the titanium: the other with $k < 1$, the OH ions (Figure 2.15). There is no interaction between these two impurities in the melt, that is the complexes are not formed in the

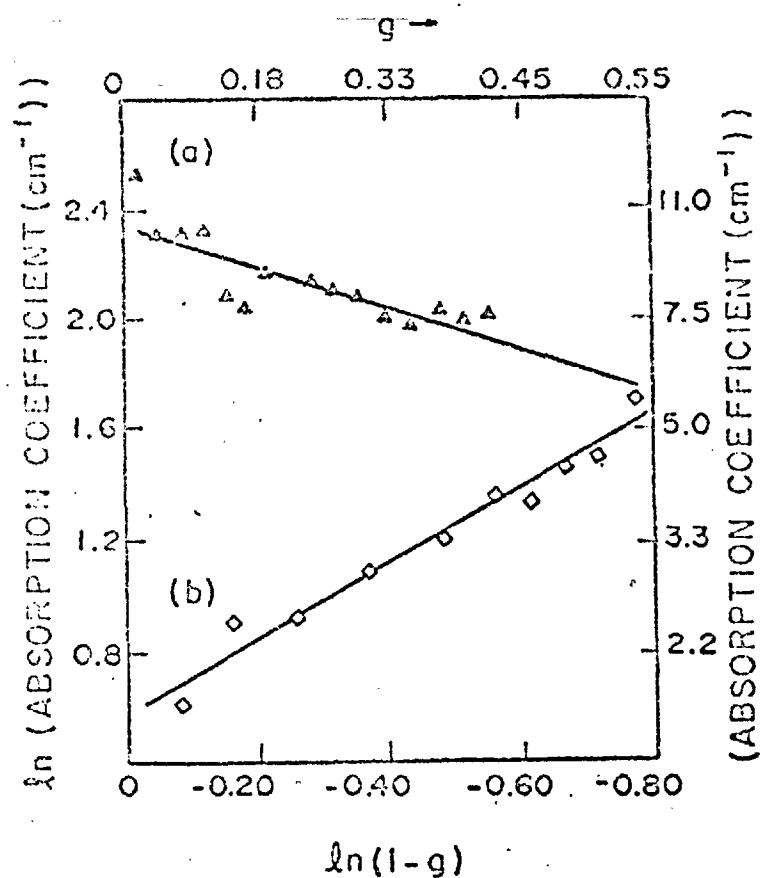
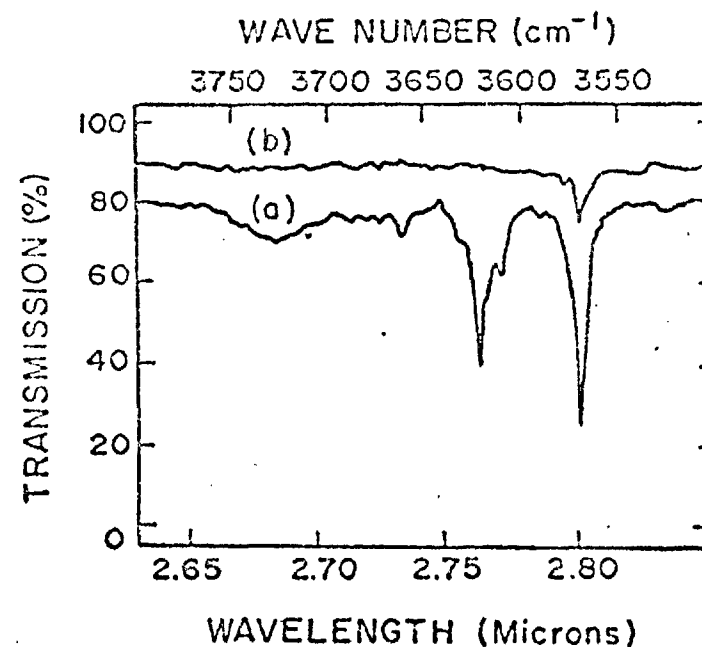


Fig.2.15. Variation of the absorption coefficient of the 200 nm band in LiF boules doped with ~120ppm Mg and ~14ppm Ti as a function of the fraction of crystal solidified (a) Baker LiF:Mg,Ti; $k=1.8$, and (b) Harshaw LiF:Mg,Ti $k=-0.3$.



Infrared absorption spectra for (a) a Baker LiF:Mg crystal and (b) a Baker LiF:Mg,Ti crystal. Crystal thicknesses are about 12mm for (a) and 10mm for (b).

melt and each impurity is incorporated in the boule as a separate entity. Hence in crystals with low OH concentrations but relatively high Ti the OH content controls the concentration of these Ti-OH complexes, as in the case of Stoebe *et al* (33). For high OH content the lower Ti content controls the concentration as in the results of Rossiter *et al* (28). The practical effect of OH on the thermoluminescent response has still to be measured. Bradbury (64) found evidence to support the existence of an OH complex but from ionic conductivity measurements concluded that although suppression of conductivity occurred in the extrinsic region above 380°C there was no preferential loss of Mg^{2+} since coincidence occurred, hence a high temperature anneal would suppress the adverse effects of the hydroxyl ion. He also failed to find absorption of OH in the infra red.

Supporting evidence for the formation of Ti-OH complexes comes from the work of Jain and Sootha (65) (see section 2.4). Making the assumption that Ti can be regarded as a divalent cation in LiF they noted that for a 100 ppm doped sample only 20 ppm of the titanium was in solution, and accounted for the other 80% as being in precipitate form which did not break up even at high temperatures so would not affect the concentration of cation vacancies. Quenching failed to disperse the impurity. The observed results are also consistent with the formation of Ti-OH complexes containing vacancies. These centres would consist of Ti^{3+} together with one cation vacancy in a nearest neighbour position; the pair would behave as a doubly charged positive titanium centre at large distances. The absence of precipitated titanium is confirmed by ESR observations in which a sharp line spectrum is observed in LiF containing 80 ppm Ti and TLD-100; if precipitation occurred line broadening should be observed.

Davies (81) recently studied titanium and titanium:magnesium doped LiF using EPR and ENDOR. The signal observed after irradiation and which he attributed to Ti^{3+} was no longer detectable following a thermoluminescent heating cycle to 300°C, although subsequent irradiation

caused the signal to return. He interpreted these results to indicate that during heating the Ti^{3+} centre captures a hole and alters the charge state to Ti^{4+} , which would not be expected to show a resonance signal. He identified the centre as Ti^{3+} displaced 0.02-0.03 nm in a 111 direction from a lithium site and postulated two models,

(i) $\text{Ti}^{3+}\text{F}_6^-$ with the Ti^{3+} off centre, (ii) $\text{Ti}^{3+}\text{F}_3\text{O}_3^{2-}$.

the latter is partially charge compensated and seems the more likely. Hole capture by the latter would cause the charge compensation to be complete.

Agreement with this model is afforded by Crittenden *et al* (82) who studied the influence of Ti on the emission spectra and concluded that the only Ti sites which can act as luminescent centres are those which trap or lose charge during the initial irradiation and revert to pre-irradiation state after luminescence. This can easily be compared with the change of Ti^{4+} to Ti^{3+} and back during the 300°C heating cycle.

Crittenden *et al* (82,83) have also demonstrated the complex nature of the defects present. In general they were in agreement with the model proposed by Mayhugh (78), that electrons released from magnesium sites interact with an intermediate defect such as a two hole trap (V_3) and release the second hole to convert Ti^{3+} back to Ti^{4+} with the emission of light (the 200 nm band).

Recent work by Fairchild (84) however, in measuring thermoluminescent emission from TLD-100 as a function of both wavelength and temperature indicates that below 10^5R the emission spectra contain three different bands peaking at 3.0, 2.9 and 2.7 eV. These results are in direct conflict with Crittenden *et al* (82) who failed to observe these three bands in their experiments. As pointed out by Fairchild though these bands could not be observed on the apparatus normally used.

2.8. Supralinearity and Sensitisation

At high dose rates supralinearity, the departure from linear relationship between thermoluminescent output and dose, and sensitisation, increased thermoluminescent output, are known to exist in TLD-LiF. Many mechanisms have been proposed to explain these phenomena (85); these generally fall into two categories assuming either an increase in the probability of charge capture at the thermoluminescent traps during irradiation or an increase in the probability of photon emission generated by thermal release of an electron from a thermoluminescent trap during the read out. A good review is given by Stoebe and Watanabe (86); it is intended here to deal with the most consistent and plausible of these which rely on the latter model being correct.

In 1968 Claffey *et al* (75) introduced the track interaction model which proposed that recombination occurred when trapped holes from one track of ionisation intersected with the F centres of nearby tracks. Zimmerman (85) has recently shown that the trapped species are in fact electrons; substitution of these for the holes of the previous model does not cause invalidation. Attix (87) has shown that it complements the model proposed by Mayhugh (78) in which he tried to relate thermoluminescence to trapping and recombination centres.

The basic proposal is that electron-hole pairs are produced during irradiation along the tracks of the secondary charged particles. Both the electrons and holes are trapped near the track; some of the centres produced along these are luminescent centres. Claffey specified F centres but this identification is not required. On heating one species of charge carriers is released and migrates to the still-trapped oppositely charged carriers and recombination occurs; if the centre happens to be a luminescent centre then thermoluminescence is emitted. For low doses the secondary electron tracks are separated far enough away so that released charge carriers only have access to the luminescent centres in the same track,

hence the thermoluminescent response against dose is linear in this region. As the dose is increased the average separation of adjacent tracks is comparable to the average separation of luminescence centres along each track. More luminescent centres are then located within the migrating range of the released charge carriers, efficiency increases and hence the output against dose is no longer linear. Most of the luminescent centres are not reached by a released charge carrier during the heating cycle and survive the read-out process; later irradiation and heating will therefore exhibit enhanced efficiency since there is an added population of centres so that sensitisation occurs.

Attix (87) explored these features and came up with the model shown in Figure 2.16. He attempts to give some form of energy budget to the thermoluminescent process and look at the mechanisms involved during and after irradiation and heating. The major difference in this refined model of track interaction is that the basic assumptions are much more general. These are: holes are the released species, although it has been shown that electrons are in fact probably the charge carriers (85) : the trapping centre is that of the Mg^{2+} cation together with a Li^+ vacancy in some form, such that the centre can be ascribed $(Mg^{2+}, Li^+-vacancy)_n$ (where n is 1, 2, 3, ...) and capable of capturing and retaining an electron or hole during irradiation. The identification of the F centre as the luminescent centre is now doubtful (38, 88) especially since the importance of the role of titanium has been shown (see previous section). It is possible, however, that the F centre combines with the titanium to constitute a complex luminescent centre as proposed by Christy and Mayhugh (14) and recently reiterated by Crittenden *et al* (82,83). Based on the previous work of Claffey, Dobson and Midkiff (89) formulated a mathematical model whose physical interpretation gives results that are in agreement with those of Attix.

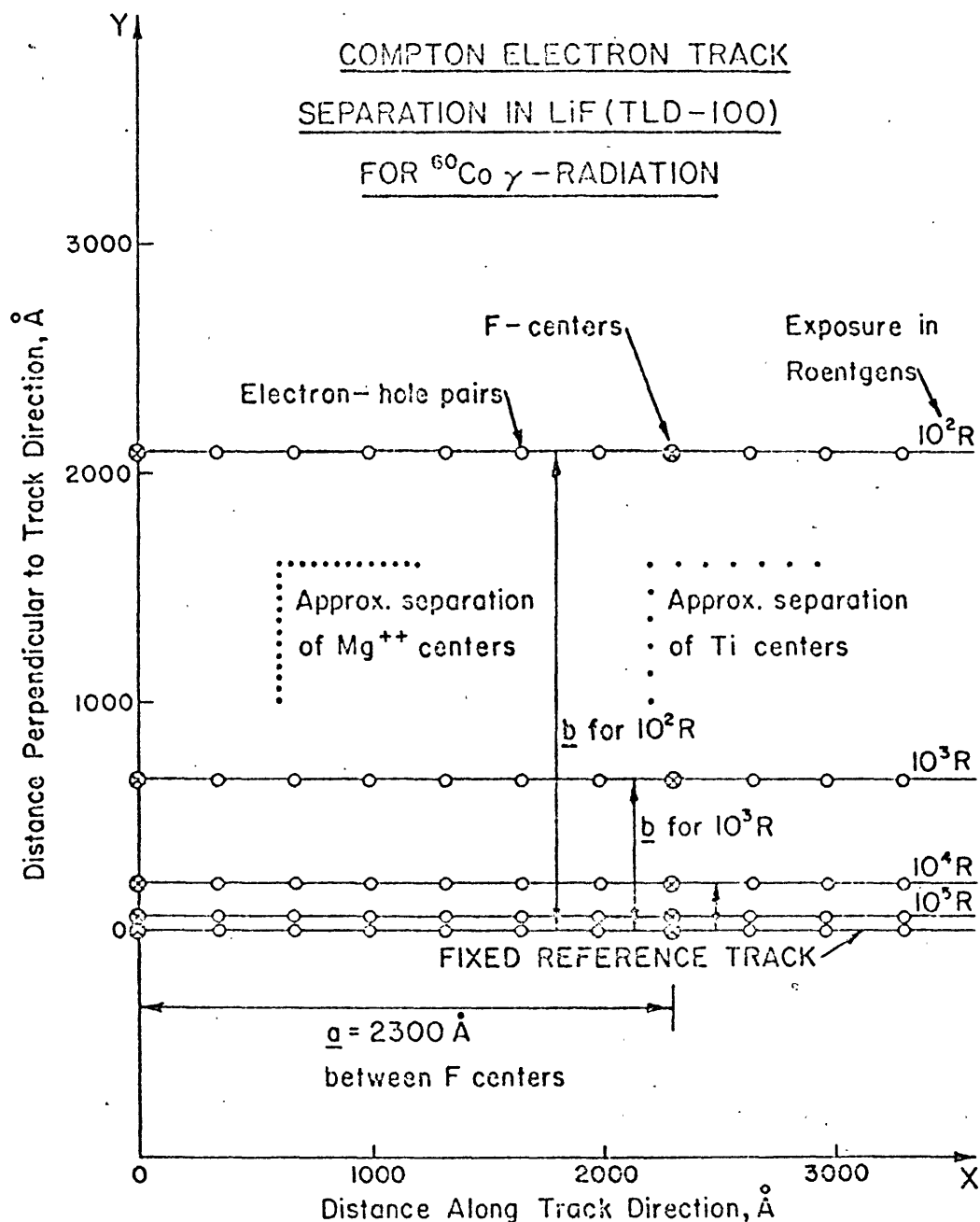


Fig.2.16.

Schematic diagram of the separation of Compton-electron tracks at various levels of ^{60}Co γ -ray exposure in LiF(TLD-100). This diagram can be imagined lying in the x-y plane of Fig. 1. The tracks are 10^7Å long. The electron-hole pairs are indicated by O, and the F-centers by $\odot$. The spacing of the Mg^{++} centers (with associated Li^+ vacancy) and Ti centers are also shown. The lattice constant in LiF is about 4Å ; the space between adjacent Li^+ and F^- ions is therefore 2Å , and they are too close to be indicated in the diagram.

2.9. Summary

In the introduction two questions were posed. As can be seen, some attempt has been made, especially in recent years, to provide answers with the result that several different models and mechanisms have been postulated. As yet no independent verification has been forthcoming although several of the proposed models do compliment each other. (For example, that of Mayhugh and Attix.) However, Fairchild *et al* (84) have recently pointed out that the emission spectra are also a function of wavelength and that this consideration has been overlooked by previous workers who have assumed emission to come from only one centre when in fact three or more such centres must be taken into account. The maxima for different peaks can be altered by the wavelength chosen, peaks 2 and 3 being different from 4 and 5. Similar work by Crittenden *et al* (82) failed to confirm this.

There does, however, seem to be some agreement as to the general principles involved. Thermoluminescence involves the interaction of ionising radiation with trapping and recombination centres which are intimately related to the impurity content of the LiF matrix; the exact nature of these centres is still uncertain. As shown the simple early theory that magnesium was responsible for the trapping and titanium for recombination has had to be modified. Recent research has also included the effect of dislocations on the thermoluminescent process (90, 91).

The major difficulties in interpretation of results arise from the instrumentation. Fairchild has pointed out that the emission spectra can be altered quite markedly by incandescence from the heater. There also appears to be quite a wide discrepancy in the reported absolute temperature values for the different peaks, see Table 2.1. which cannot be accounted for by the different heating rates. It is possible that the considerations of thermal conductivity and in the case of polycrystalline material, grain boundaries, have been overlooked. Depending on the

TABLE 2.1.

Investigator	Peak	Temperature °C.
Cameron <i>et al</i> (35)	2	105
	5	190
Klick <i>et al</i> (69)	5	210
Attix (87)	2	100
	3	130
	4	180
	5	210
Harris and Jackson (72)	1	65
	2	120
	3	160
	4	195
	5	210
Murali Dhara Rao (74)	1	75
	2	100
	3	130
	4	175
	5	200
Bradbury (64)	1	65
	2	110
	3	150
	4	180
	5	200

position of the monitoring thermocouple the temperature is bound to alter, thus an apparently low temperature can be ascribed to the peak. Only one group of workers, Jackson and Harris (73, 92, 93) state that the temperature is that of the pan. Monitoring of the emission spectra in a wide wavelength range will also give ambiguous results in that extra peaks will appear as 'bumps' on the side of existing peaks due to the overlooking of the fact that the spectra are also a function of the wavelength.

Most of the recent work reported here has been on single crystals of TLD-LiF, either the commercial TLD-100 or specially grown material of known impurity. There is ample evidence that concentration gradients produced during manufacture exist such that ambiguous results can be obtained. Although sectioning of the material and separate chemical analysis can overcome this difficulty when dealing with the small impurity levels thought to be present there must be some element of doubt. In practical dosimetry the material is used in a powdered form or as a Teflon impregnated disc; hence it would help to try and find out whether any of the proposed models will hold for the polycrystalline material, and if not why not.

CHAPTER 3

Experimental Techniques

3.1. Introduction

In order to investigate the thermoluminescence of LiF a suitable source of material had to be found. Since the initial part of the work was in conjunction with the findings of NPL, material grown by their technique was used. This was then characterised by chemical analysis, ionic conductivity measurements and microhardness tests. A compacted LiF dosimeter was produced by vacuum hot pressing of the powdered crystal; this was subsequently irradiated and read out.

3.2. Preparation of Material

(i) Crystal Growth

Crystals of TLD-LiF were grown by the Bridgman technique developed by NPL (26). This enables a 60 gram crystal 2.00 cm in diameter by 8.00 cm in length of known starting impurity level to be grown, Figure 3.1. The crucible is made from reactor grade graphite (available from Morganites) and machine tooled to produce the conical tip. This is suspended in an alumina support frame which is allowed to hang freely on the support wire, thus allowing the whole crystal to be used. Previously the support wires were suspended through the crucible and hence the top 0.8 cms had to be discarded. Furnaces were constructed from mullite tubing and heated by nichrome wiring so as to produce two uniform-temperature zones, each 12 cms in length, Figure 3.2. The upper furnace is at 50°C above the melting point of LiF, the lower at 50°C below. LiF melts at 870°C. The whole system is flushed with Argon at 0.35 litres/min.* The crucible is placed in the upper part of the zone for about 4 hours to ensure complete melting of the material, then lowered through the lower furnace at 2.19 mm/hour. On reaching the lower limit the lower zone is gradually reduced to that of ambient over a period of about 8 hours. The only refinement required to the

*No extra drying agent for the Argon was used.

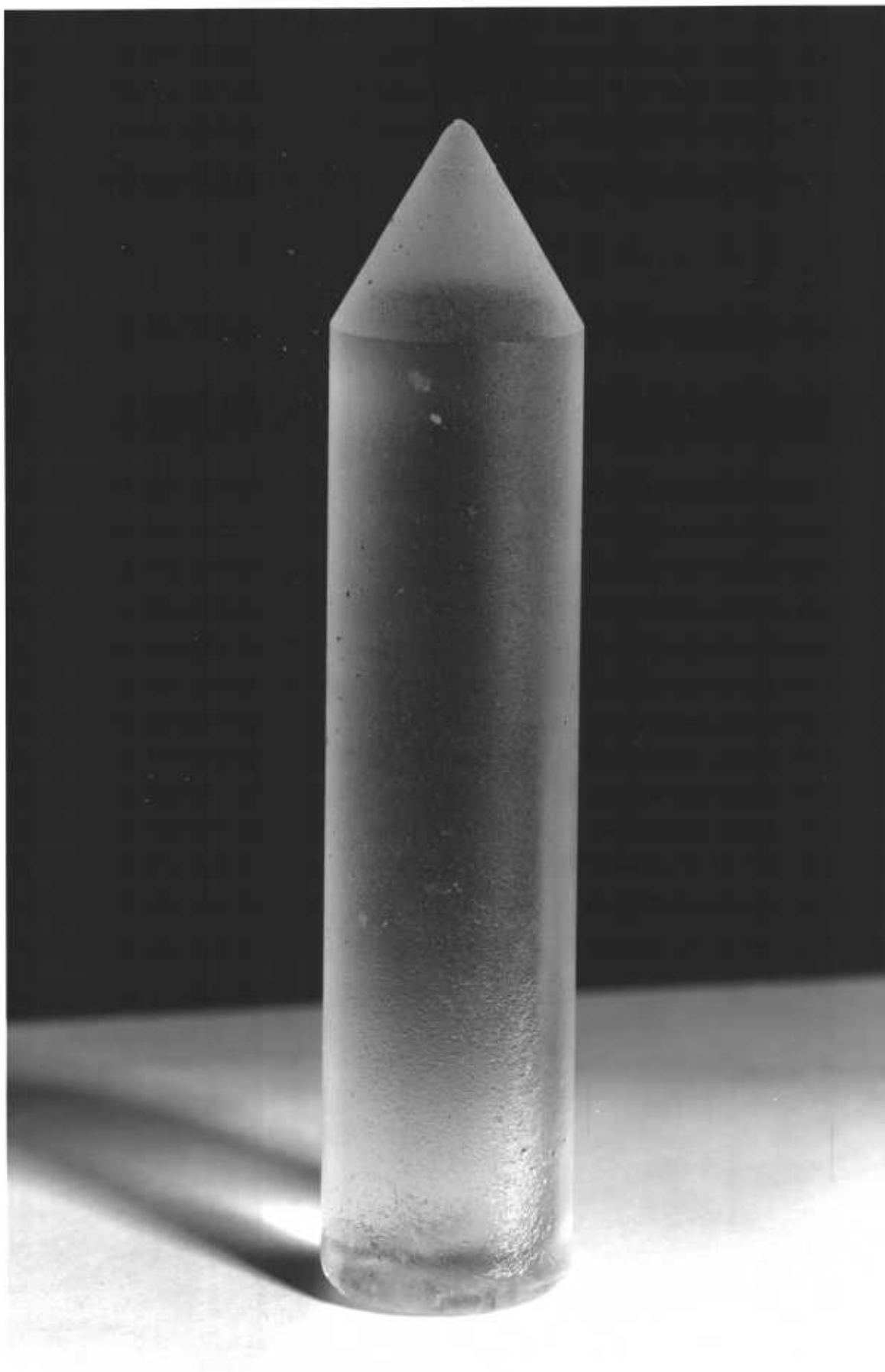


Figure 3.1. Grown Crystal.

crystal is immersion in nitric acid after removal from the mould to clean off any graphite surface layer that might be present.

(ii) Polycrystalline LiF

There are two basic techniques available for the formation of a ceramic compact, namely sintering and 'hot pressing'. The former involves the pressing of the material followed by an annealing procedure at some suitable temperature which will allow densification of the compact. Several models exist to explain the phenomena involved (94). The latter technique involves carrying out the pressing at some stated (elevated) temperature, usually in a vacuum or inert atmosphere. In this case the main mechanisms for densification are those of diffusion and plastic flow (95). If correct pressing conditions for the material can be obtained then near theoretical density can be achieved.

The LiF grown and that supplied by the chemical companies is in the form of single crystals. It has already been shown that although single crystal work can characterise the material it does not allow for standardisation; production of a homogeneous material can however be obtained by crushing the single crystal. The easiest and best method for doing this is by the simple technique of an agate pestle and mortar. In this way any contamination is kept to a minimum since the only substance that the crystal will be in contact with is that of the agate. Consequently the LiF crystals that were grown were ground and passed through a series of sieves ranging from 100 to 325 British mesh size. This gave material having^a maximum particle size within the limits 150 to 44 microns, although it was found that a preferred range of maximum particle size 73 to 53 microns (200 to 300 British mesh) gave a more translucent product.

(iii) Vacuum Pressing LiF

The technique employed here for the production of polycrystalline TLD-LiF was that of warm pressing, utilising a vacuum press designed for the pressing of polycrystalline sodium chloride by Stucke (96).

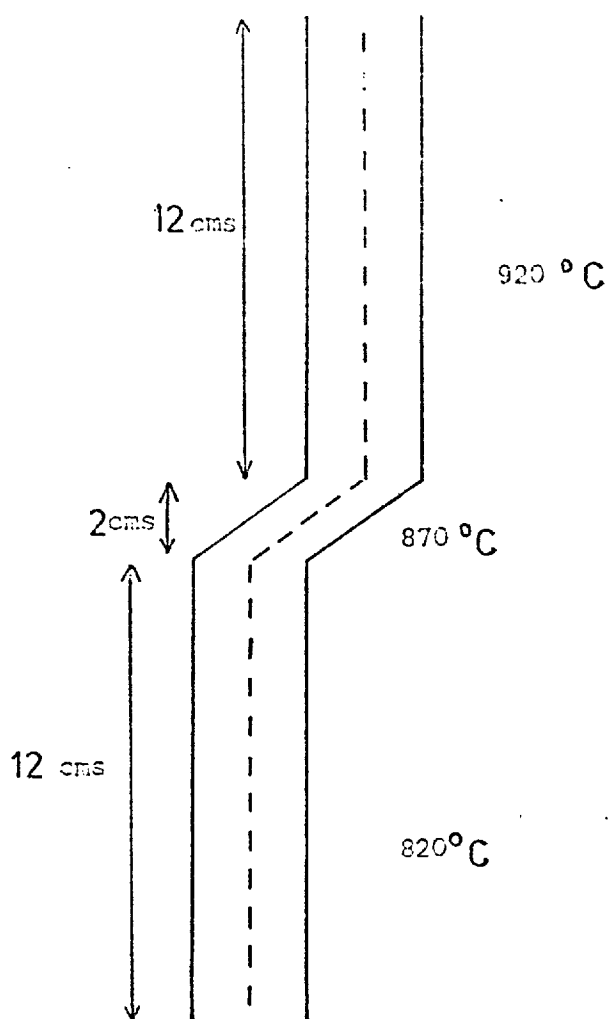


Fig.3.2. Schematic Representation of Furnace and Temperature Zones.

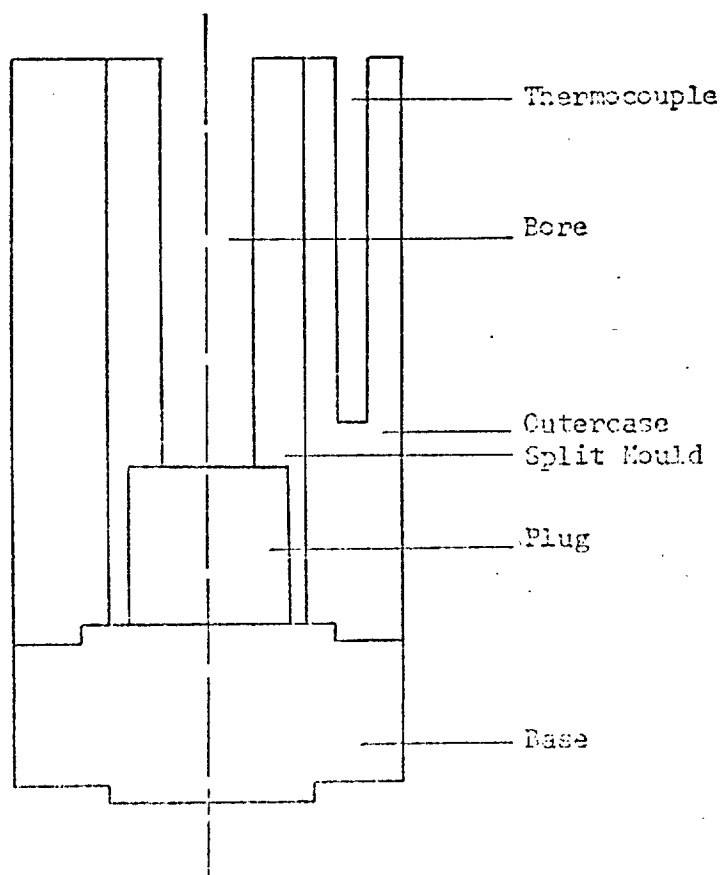


Fig.3.3. Diagram of Split Mould. (Actual size).

The main feature required in the present work was that the press should allow easy removal of the compacted pellet, so a split mould was designed. The mould is shown in detail in Figure 3.3. and a photograph of the component parts in Figure 3.4.

The outer case of the mould remained the same as that described by Stucke (96).

The inner bore is split longitudinally so that on removal of the outer case the die can be opened up and the pellet removed without any further pressure being applied. The ram is made of high tensile En 24 steel and graphite spacers are placed on either side of the powder to prevent chilling of the pellet and to facilitate lubrication. A limitation to the operating temperature was caused by the choice of die material since the temperature must be kept below 700°K, but since one of the objectives was to try and produce a dosimeter under fairly practical conditions, that is reasonable temperatures, there seemed little point in using a higher grade material.

The press was heated by the original furnace which is of nichrome resistance wire vertically wound on an alumina tube, electrical connections being made by a ceramic lead-through in the base plate and the temperature monitored by a chromel/alumel thermocouple. The whole system was enclosed in a water-cooled vacuum tight cylinder, attached to a vacuum pump system capable of maintaining a pressure at the pump of less than 10^{-2} N/m² (10^{-4} mm of Hg). The load was applied by a standard 10,000 kg Instron testing machine. The press was mounted on the crosshead whilst the ram was pushed using a compression load cell mounted in the top frame. The load was applied on a continuous cycling for one hour after the temperature of the pressing had been reached.

Preliminary tests (97) showed that ideal conditions for near maximum theoretical density were a pressure of 500-300 MN/m² at a temperature of 275°C. The pellet obtained was translucent and had a density of 99.5%. This was then cut with a Capco diamond blade to obtain discs of 0.75 cms

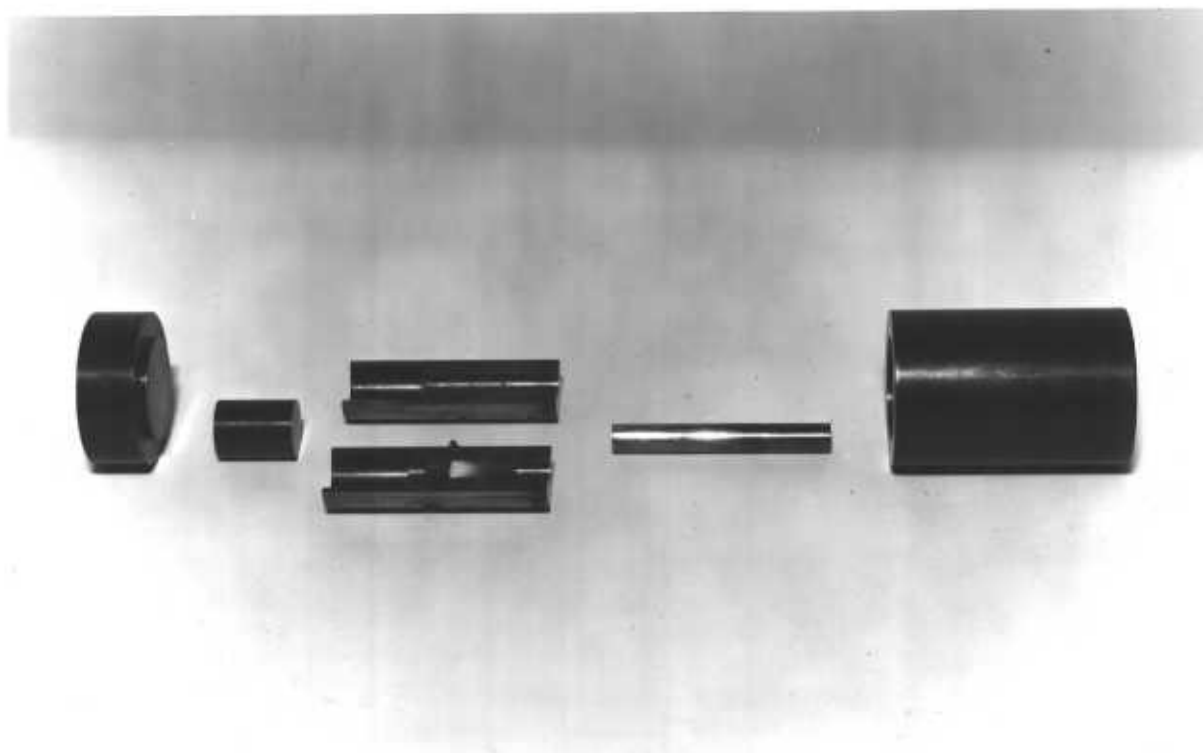


Figure 3.4. Split Mould.

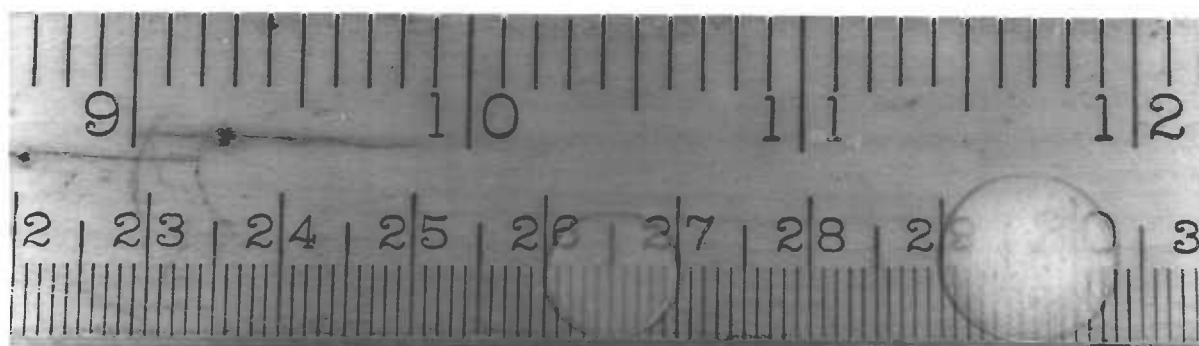


Figure 3.5. Polycrystalline Dosimeter Discs.

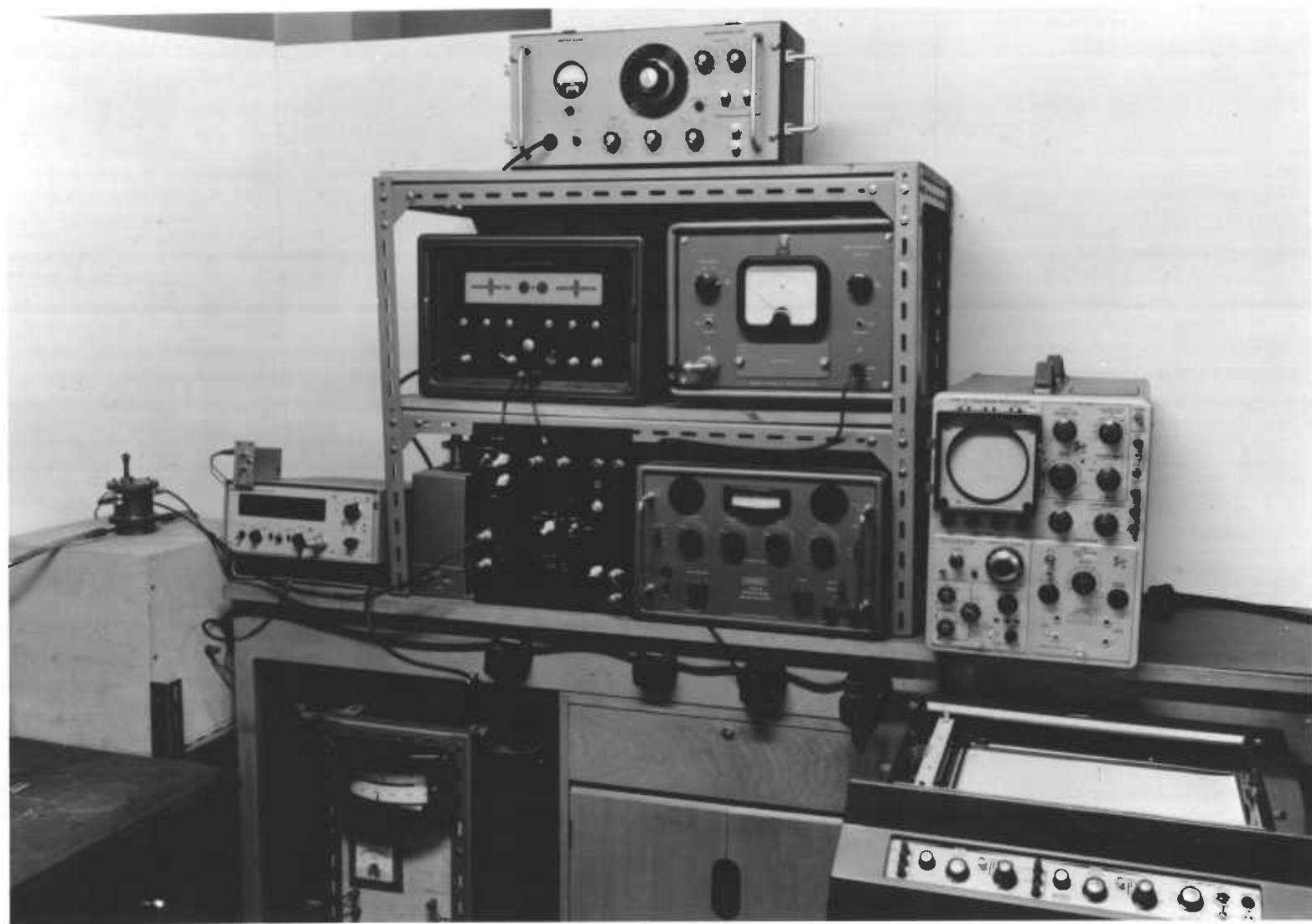


Figure 3.6. Ionic Conductivity Apparatus (Overall View).

thickness, Figure 3.5. The design of the split die made it possible for pellets of different diameters to be made varying from 0.825 cms to 1.27 cms. It was found that the smallest of these was the most convenient for dosimetric use.

Density of the pressed TLD-LiF pellets was measured absolutely. The volume was found by rubbing down the two flat faces so as to make them square to the axis of the pellet then measuring the height and diameter using a micrometer screw gauge reading $\pm 1 \times 10^{-6}$ m. Several readings of each measurement were made and the mean value taken so as to minimise experimental error.

The weight of the pellet was found using an electronic chemical balance weighing down to $\pm 1 \times 10^{-5}$ g. Successive density measurements on one pellet showed agreement between results of $\pm 1 \times 10^{-3}$ kg/m³, i.e. $\pm 0.05\%$. Density of the pellet was expressed as a percentage of the theoretical density of single crystal LiF, 2.635×10^3 kg/m³.

3.3. Ionic Conductivity Measurements

A.C. ionic conductivity measurements were carried out using the apparatus shown in Figure 3.6. It is possible to evacuate the furnace but this causes evaporation problems so that in all experiments oxygen-free nitrogen was passed over the specimens. The examination of the polycrystalline material was carried out on 0.95 cm diameter dosimeters since these fitted the surface area of the electrodes; for single crystals comparable size specimens were cleaved along the (100) faces.

The conductivity rig itself is shown in detail in Figure 3.7. The stainless steel electrodes are supported on rods, being held in position by a P.T.F.E. insulator at the top of the furnace. The electrodes are shielded from the furnace windings by a stainless steel tube which also forms part of the vacuum tight envelope. Nitrogen was passed through the system to prevent oxidation of the electrodes and contamination of

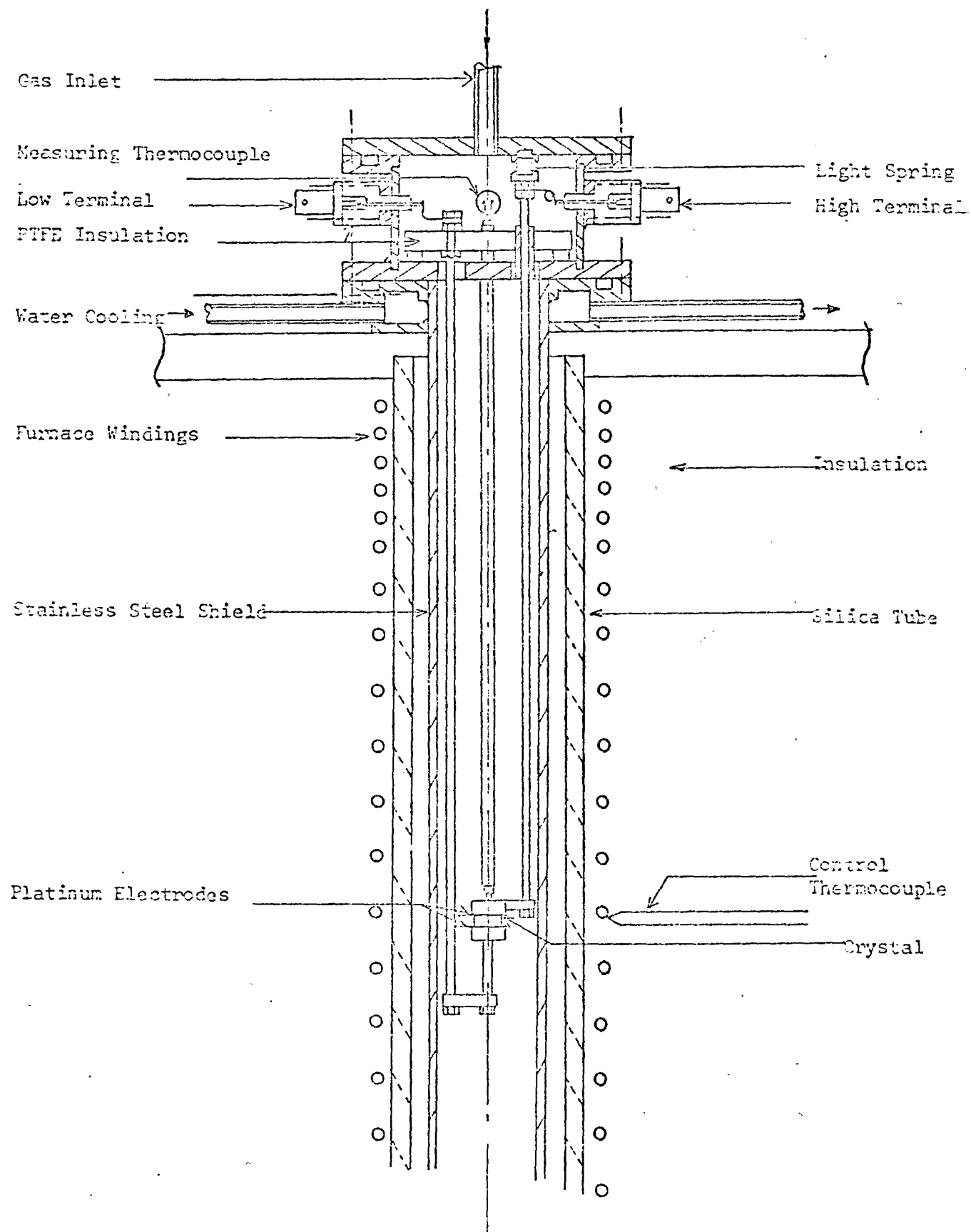


Fig.3.7. Ionic Conductivity Rig.

the specimen. Electrical connections were made *via* screened connectors as was the connection to the Chromel/Alumel thermocouple. The specimen is kept in intimate contact with the electrodes by the use of a light spring which applies a small load to the high electrode, Figures 3.8 and 3.9. The rig is heated by a nichrome wound resistance furnace, the power to the furnace being supplied by a smoothed d.c. 220 volt supply to minimise a.c. pick up in the conductivity circuit; since the method of measuring the conductivity is by means of a Wayne Kerr Bridge utilising an a.c. current, this minimises any polarisation effects. The temperature of the furnace was found to reach equilibrium quite rapidly which is important since there is an exponential conductivity time decay. There are two ways of measuring the conductivity on the apparatus described; either taking the readings and increasing the temperature, or taking the rig up to temperature and taking the readings as the temperature is decreased. At higher temperatures the specimen will tend to soften and better electrode contact can be made since surface irregularities will be counteracted. For this reason the rig temperature was raised to 800°C and left to equilibrate for 24 hours. Readings were then taken every 5° to 10°C as the temperature was lowered.

3.4. Irradiation

Irradiation of specimens was carried out in the main ⁶⁰Co- γ -ray source at Imperial College; γ -irradiation was chosen as being the most efficient and easiest to control. (Soft X-rays would have meant a long exposure time and TLD-LiF is subject to the Law of Reciprocity.) Although the specimen as a whole is irradiated to a relatively low exposure there is often superficial high exposure; hence ^{the} thermoluminescent response will be that of the surface not the bulk. Compton and Schulman (98) found an increased microhardness in the surface layer after irradiation. More important though in thermoluminescence studies is the fact that

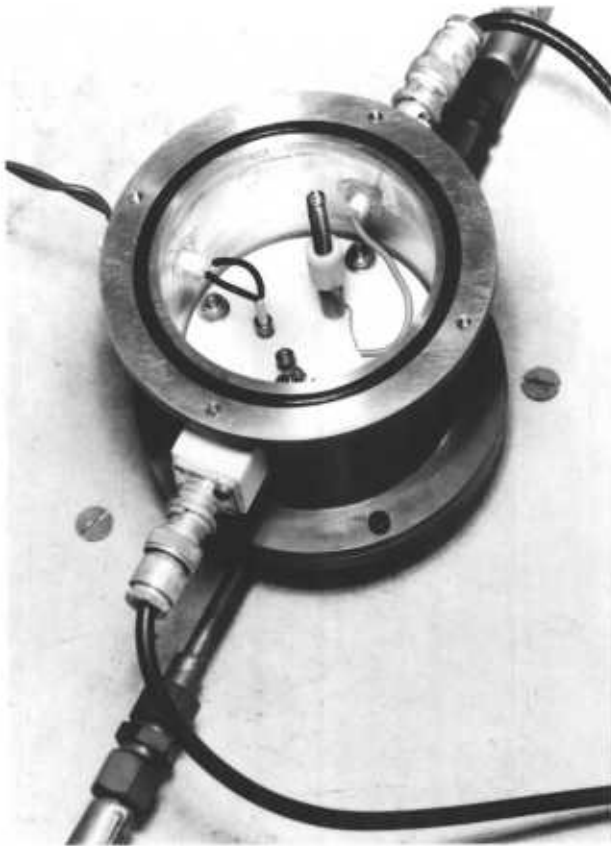


Figure 3.8.



Figure 3.9.

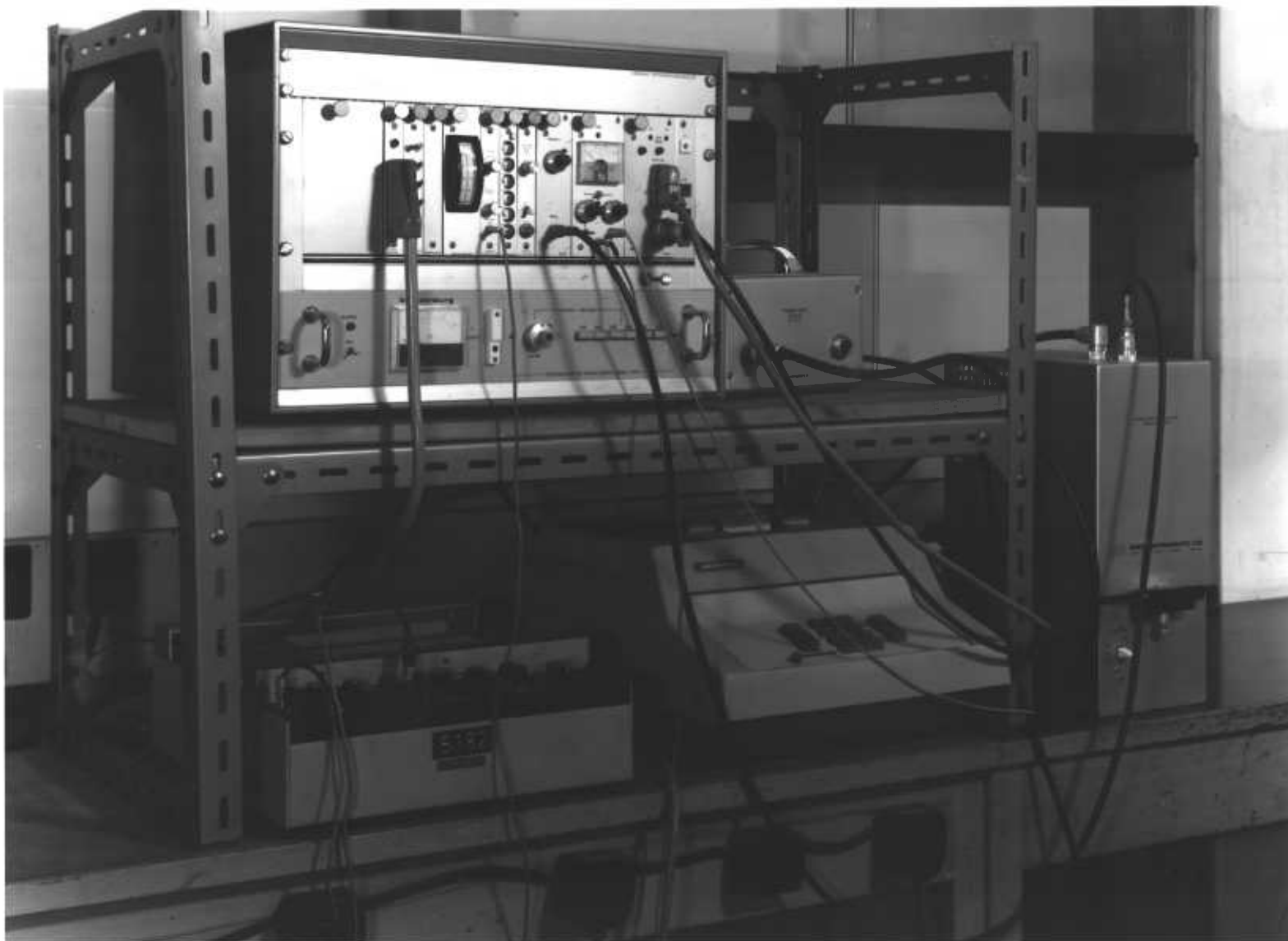


Figure 3.10. Thermoluminescent Read Out Unit.

anion interstitials and anion interstitial clusters (43, 44) may be formed near the surface of the crystal and compete with the thermoluminescent trapping and recombination centres as electron and hole traps. Since the work involved here required numerous repeated exposures, problems could easily have arisen but because of their high energy and almost monochromatic nature of ^{60}Co - γ rays these problems do not exist.

Readings were made 15 minutes after irradiation so that the decay of the peaks was uniform. Peak 1 was ignored. A dose of 400 rads (absorbed dose) was given to the specimens by exposing them for 4 seconds to one of the six source rods. The specimens were placed in 'A' cans which allowed the effects due to build up to be neglected; this was especially important for the small specimen dimensions used. An independent check was carried out by the conventional chemical method and confirmed the dose rate.

3.5. Thermoluminescent Read-Out Unit

The thermoluminescent read-out unit is that shown in Figure 3.10. A schematic diagram is represented in Figure 3.11. The apparatus consists of an EKO N.141 photo-multiplier tube connected to Harwell 6000 series electronics. The principle features are the linear heating-rate which was independently checked and the filter involved in monitoring the thermoluminescent output from the specimen to the tube. The photomultiplier in this case is fitted with a quartz window which is very transparent to ultra-violet and visible light, becoming opaque beyond 7,000 nm. Thus any incandescence from the heater in the infra-red region would be picked up if correction filters were not fitted. The abscissa of the glow curves can either be plotted as temperature or since the rate was linear, time. For the purpose of production of smooth glow curves the latter was used since 'pick-up' on the temperature terminals led to spurious peaking.

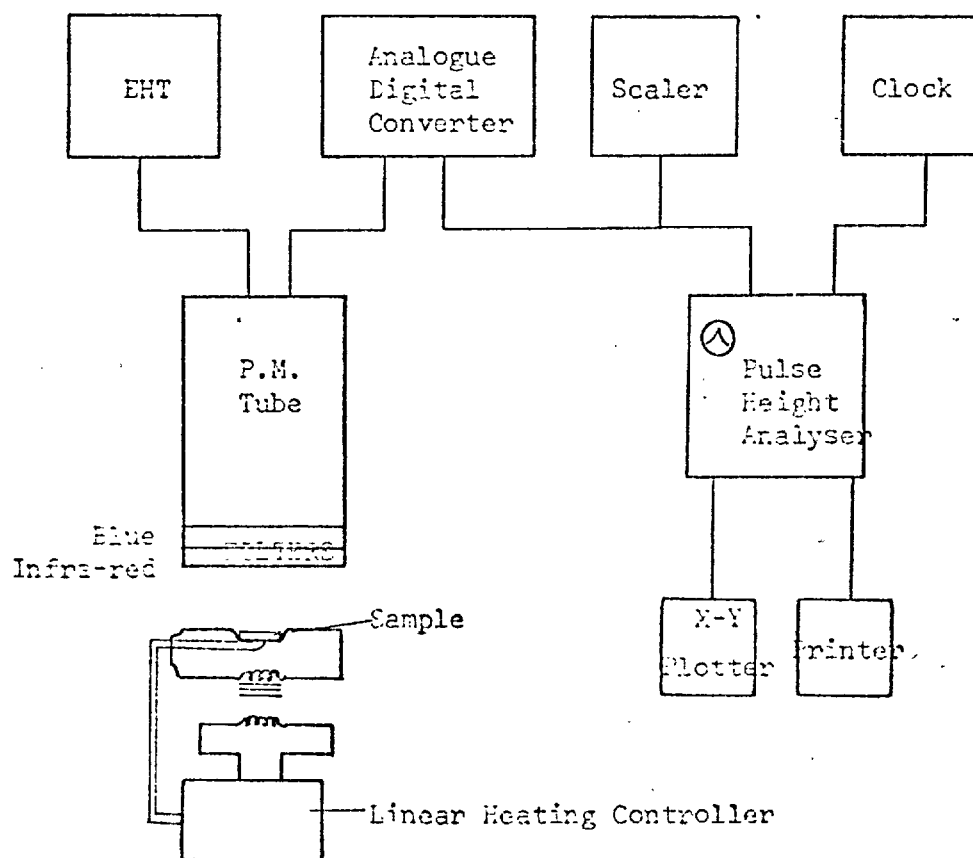


Fig 3.11. Block Diagram of Glow-Curve Read-Out Apparatus.

The specimen is placed in the planchette and then slotted under the photomultiplier tube. It is then raised so that a plaited wire heater is positioned above and below. The thermocouple is connected to the lower heater and to the rate-meter. In order to check the temperature of the specimen a separate thermocouple connection was made at the planchette perimeter; this was then monitored. The results confirmed that the heating rate was linear and also that a thermal conductivity lag due to surface contact existed.

Although many workers pass nitrogen through the system during read-out, independent tests on the NPL system (on which our system was modelled) proved that this was not necessary.

3.6. Other Methods of Characterisation

(i) Microhardness

Microhardness testing was carried out on a Reichert microscope, a special plate being made to accommodate the small dosimeters. The hardness is defined as the load acting on the indenter divided by actual surface area produced by this indentation. The value is expressed in terms of the Vickers Hardness number. Values were obtained for the single crystal and polycrystalline dosimeters both before and after irradiation.

(ii) Chemical Analysis

Chemical analysis was carried out by the analytical services department using atomic absorption measurements. Values were obtained for the magnesium concentrations but that of the titanium was less than the limits of detectability, in this case 10 ppm. X-ray fluorescence was also inadequate for the titanium. An EPMA run was performed on the longitudinal dimension of the pressed pellet to see if any differential concentration gradient existed due to pressing. Again the limits of detection were such that the only information obtainable was that there was no obvious specific region of high concentration.

(iii) Photomicrography

In order to determine the particle size of the dosimeters micrographs of polished and etched specimens were made. Polishing was done using γ alumina powder and hydrogen peroxide 20% volume was used at the etchant.

Characterisation4.1. Chemical Analysis

Crystals were grown from Optran Zone-refined LiF (BDH Chemicals Ltd.) by the technique described in Section 3.1. Additions of Magnesium were added as Optran MgF_2 (BDH Chemicals Ltd.) in the range 0-400 ppm. Table 4.1. gives the mass spectroscopic analysis of the starting material as supplied by the manufacturers. Since the only parameter being altered extrinsically is that of the magnesium content, all crystals being grown from the same quality controlled batch, chemical analysis of the material was confined to investigation of the magnesium content. Originally it was hoped to monitor the Titanium concentration but the quantities involved proved too small for the techniques employed for any meaningful results to be obtained. The compositions are shown in Table 4.2. Analysis of the starting material before and after crystal growth was also carried out. This was especially interesting since the thermoluminescent response is different, as will be discussed later. It would appear that the material is 'picking-up' magnesium contamination sometime during the preparation and growing stages. One would expect that any effects of 'zone-refining' produced by the method of crystal growth to be negated on crushing the crystal prior to dosimeter production.

In future discussions the 'nominal' additive of MgF_2 compound will be used, hence 50 ppm refers to a crystal containing the impurities as described in Table 4.2(ii). There has, in the past, been much confusion resulting from the inability of authors to state exactly what impurity criteria they are using, *i.e.* Magnesium or MgF_2 compound. As can be seen this leads to a factor of approximately 2 in the critical dopant levels. Table 4.3. summarises this, giving the results of analysis of TLD-100.

TABLE 4.1.

Mass spectroscopic analysis of Optran LiF (as supplied by BDH Chemicals Ltd.)

Element	Ti	V	Sc	Ca	K	Cl	P	Si	Mg	Na	B
ppm(atomic)	2.6	<0.2	<0.2	<2	<0.2	80	<0.2	<4	6	0.2	0.8

TABLE 4.2.

Additions as MgF_2 . Figures for analysis are given both as the compound MgF_2 and the element Mg.

Analysis	ppm Mg(± 4)	ppm MgF_2 (± 10)
Nominal	Found	
(i) 0	16.25	42.5
(ii) 50	32.5	85.0
(iii) 100	56.875	147.5
(iv) 200	102.5	262.5
(v) 400	176.875	453.75

TABLE 4.3. Analysis of TLD-100.

'Quoted Mg ppm'	Ti ppm	analysis	Investigator
110	6	spectrographic	Miller & Bube (88)
200	15		Stoebe & Watanabe (86) 1975
125		quantitative spectroscopy	Claffey (68)
100	15		Attix (87)
100		quotes ref. of Grant & Cameron (wrong)	Klick <i>et al</i> (69)
110 mf			Dryden & Shuter (31)
230 mf			Vora, Jones, Stoebe (32)
400 (100) wt	4(8)		Becker, Cheka, (105) Oberhofer

4.2. Ionic Conductivity

Ionic conductivity plots were obtained for all five ranges of dopant levels investigated in both the single and polycrystalline form. (see page 33)

The Activation Energies for stage II, Q_{II} , are summarised in Table 4.4. Figures 4.1(i) and 4.1(ii) show the consolidated plots of these, together with a TLD-100 single crystal sample.

Within the limits of experimental error, i.e. $\pm 5\%$ the stage II activation energy for both forms of the material give good agreement with other investigators in the field (99,100), the value calculated here being 0.76 ± 0.03 eV. There could, however, be a tendency towards a slightly higher activation energy (0.76 - 0.78 eV) with increasing dopant levels; some investigators (66) have reported this but not too much significance should be attached to these results since the techniques for absolute measurements have not yet been perfected.

Although Figures 4.1(i) and 4.1(ii) would seem to show a definite Stage I and hence calculatable Q_I Activation Energy it must be pointed out that the 'Knee' of the Arrhenius Plot lies on a gradual curve and hence attempts to extract manually an activation energy for Q_I led to arbitrary results. Computer programs do exist for obtaining valuations of this sort but they have not been implemented in the present research, the main reasons being that only relatively few readings were obtained at the top end of the temperature range and hence meaningful results would be difficult to obtain. For similar reasons the association region III, although beginning to become obvious on the plots, cannot really yield any meaningful analysis. That association is occurring would seem to be shown, but to what degree and the calculation of the energies involved has not been attempted. The more dopant present, the more marked association becomes.

The magnesium increase is clearly shown in the single crystal specimens. (Figure 4.1(i)). With the exception of the 50 ppm sample the curves show

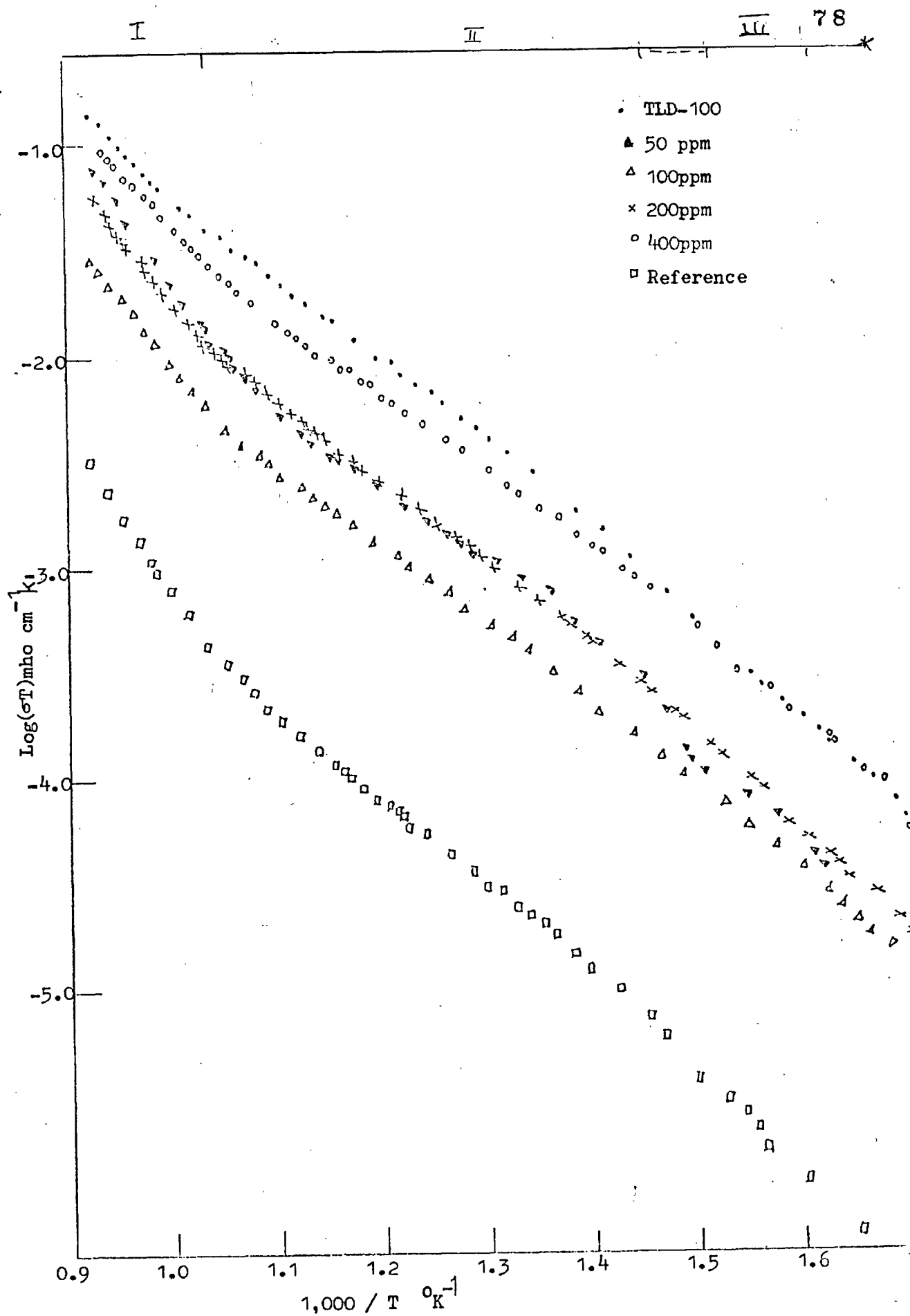


Fig.4.1(i). Consolidated Ionic Conductivity Plots for Single Crystals.

* (cf Fig 2.5 page 34)

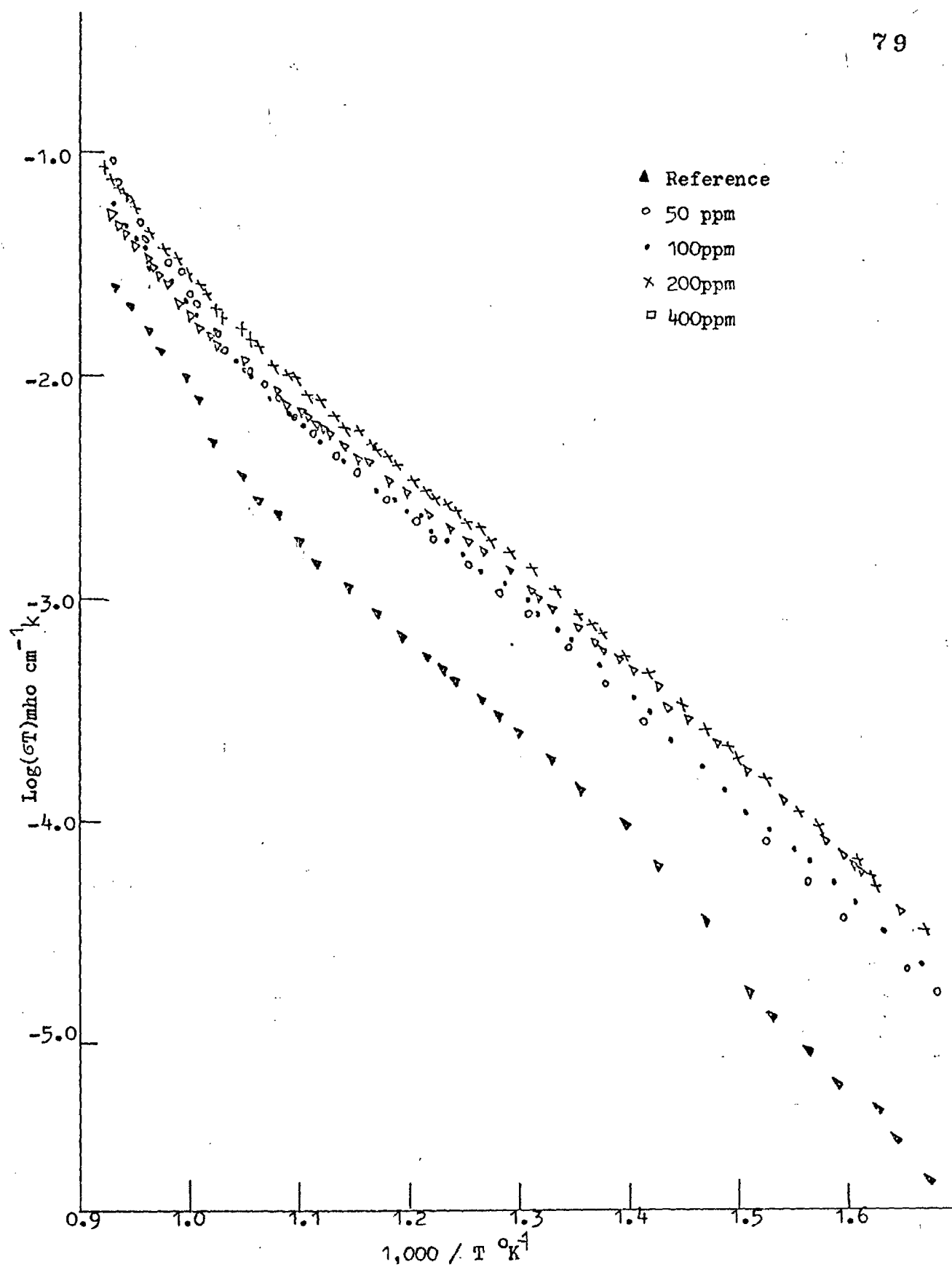


Fig.4.1(ii). Consolidated Ionic Conductivity Plots for Polycrystalline Dosimeters

TABLE 4.4. Activation Energies.

Reference		Q_{II} (eV)
	Single	0.76
	Disc	0.82
50	Single	0.66
	Disc	0.8
100	Single	0.76
	Disc	0.76
200	Single	0.76
	Disc	0.76
400	Single	0.66
	Disc	0.78
Titanium	Disc	0.78
TLD-100	Single	0.78

The accuracy of $\pm 5\%$ is equivalent to a value for Q_{II} of 0.76 ± 0.03 eV.

This compares with the value of 0.7 ± 0.02 eV from Stoebe and Pratt

(included in the results in Fig. 2.6 page 34) and that of 0.76 eV from Johnson (100).

the predictable increase in conductivity with increasing concentration, thus affording a check on the magnesium concentration, since the conductivity σ , is proportional to the charge, the mobility and concentration. The first two must remain constant for the stage involved hence the increase/decrease in conductivity is a measure of the concentration. The results are more difficult to interpret for the polycrystalline material, Figure 4.1(ii), since there seems to be some grain-boundary effect that masks the increase in conductivity due to the increase in magnesium.* Analysis of the concentrations by the method described above would not yield results in agreement with those obtained by conventional chemical analysis as occurred in the single crystal specimens.

Comparison of Figures 4.1(i) and 4.1(ii) would seem to indicate that the activation energy for the migration of cation vacancies is unaltered by the form of the material. Although adjustments were made for dimensional effects care must be taken during comparison of the single crystals and discs; the results should be looked on as showing a general trend.

Looking at each composition separately, Figures 4.1(iii) - 4.1(vii) the conductivity of the polycrystalline material is suppressed with increasing magnesium concentration. Since this results in the single specimen of high magnesium content having a higher conductivity whereas in the reference sample this was the complete reverse (Figures 4.1(vii) and 4.1(iii)) the effect of the grain boundaries in suppressing conductivity must be greater than that of the magnesium concentration in increasing it. Further investigation needs to be carried out on this grain boundary effect, especially in the dopant region of 200 to 400 ppm Magnesium. It is interesting to note that in all the other dopant levels the curves tend towards each other in the association region; in the 400 ppm this trend is missing.

*The effect of small but varying amounts of porosity at the grain boundaries is known to be significant in other systems.

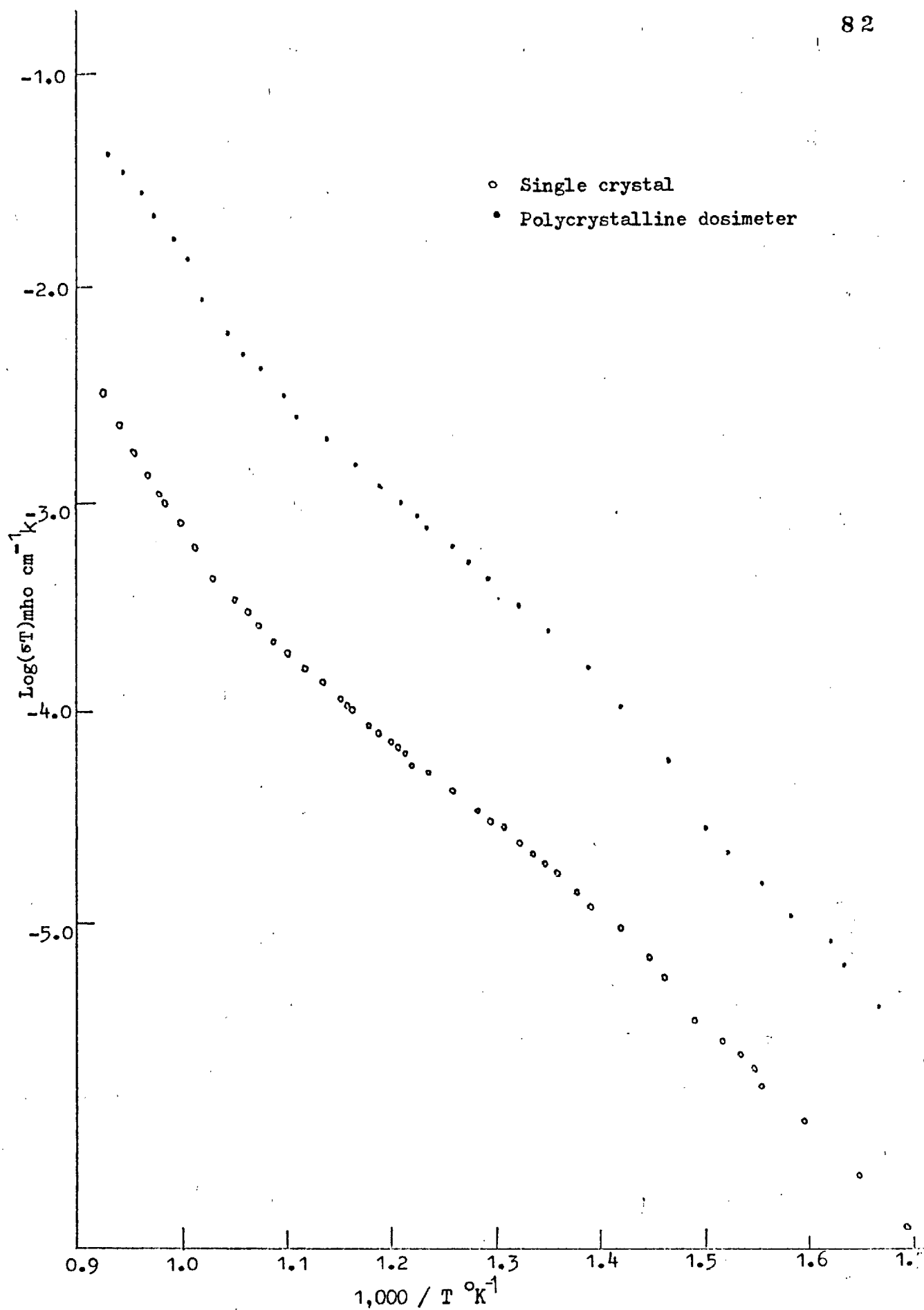


Fig.4.1(iii).Ionic Conductivity Plots for the Reference Material

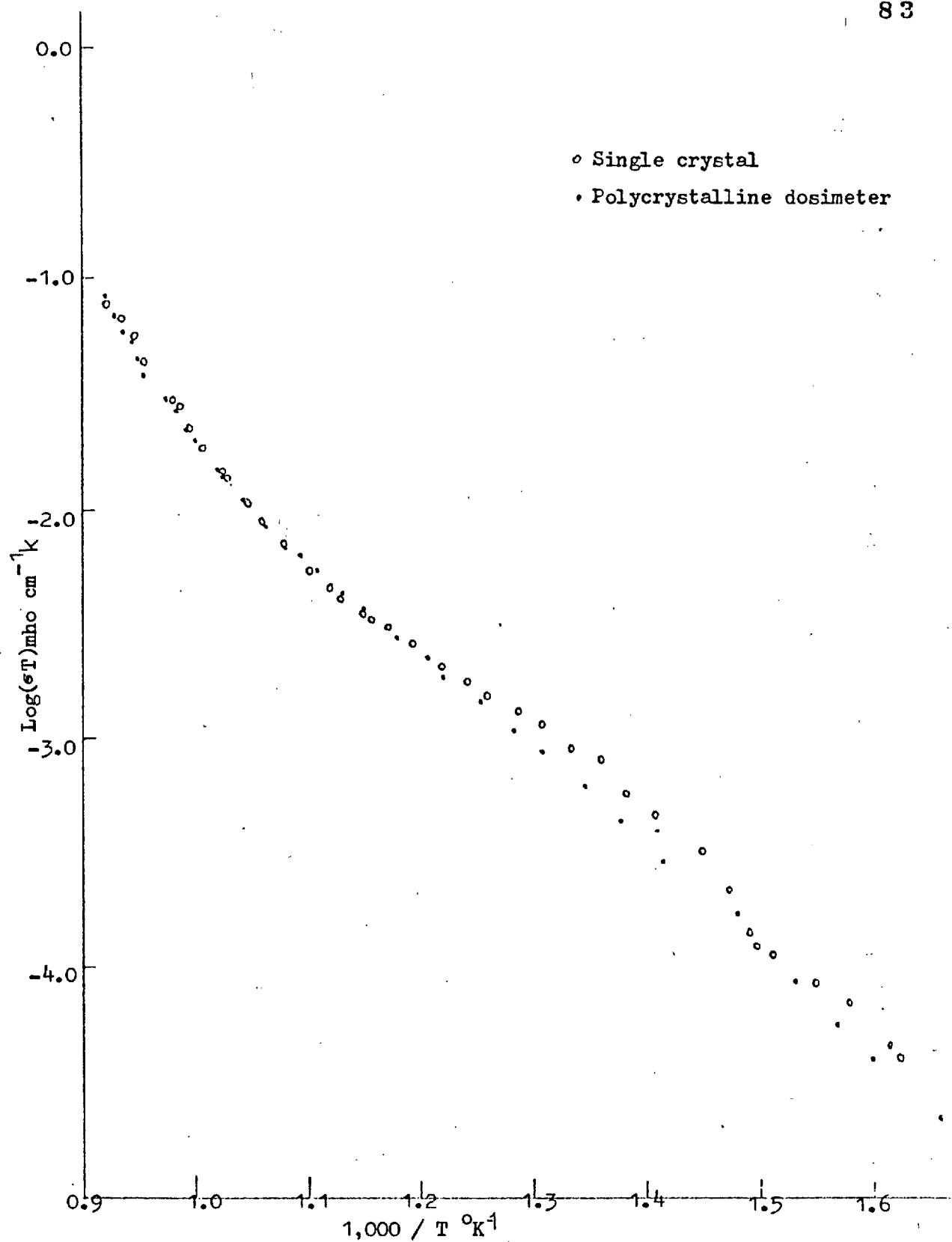


Fig.4.1(iv). Ionic Conductivity Plots for 50ppm Mg material.

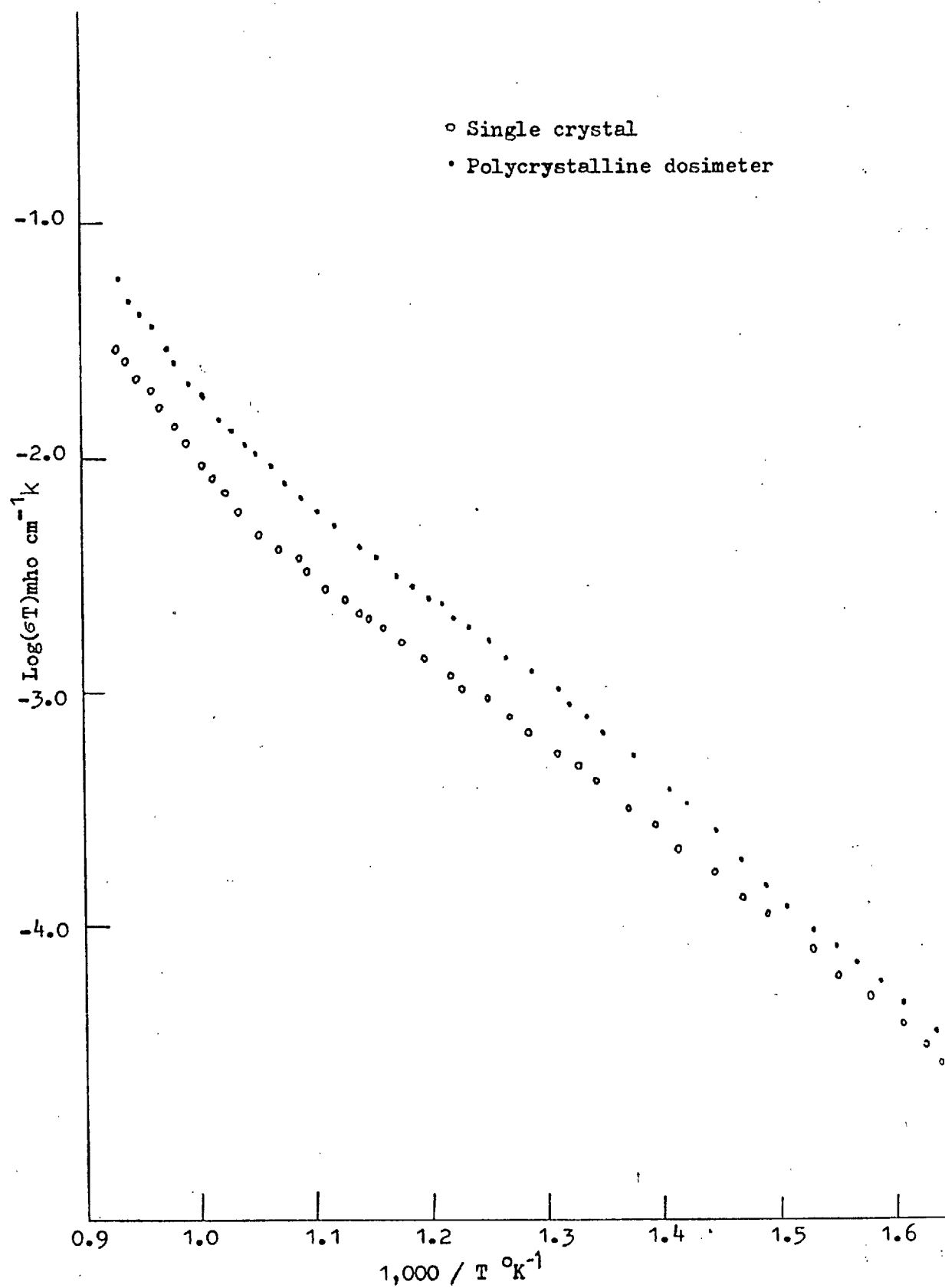


Fig.4.1(v).Ionic Conductivity Plots for 100ppm Mg Material.

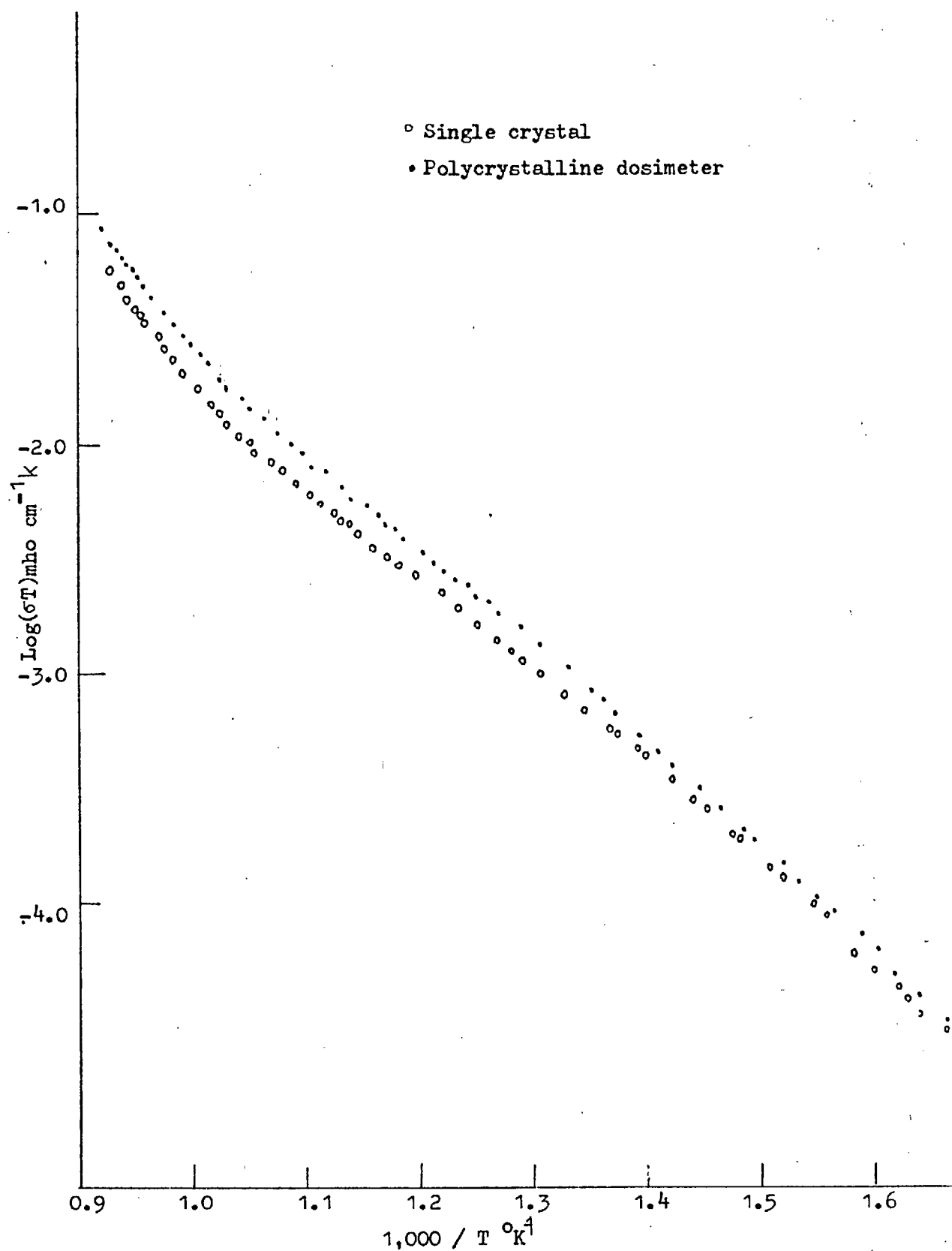


Fig.4.1(vi).Ionic Conductivity Plots for 200ppm Mg Material.

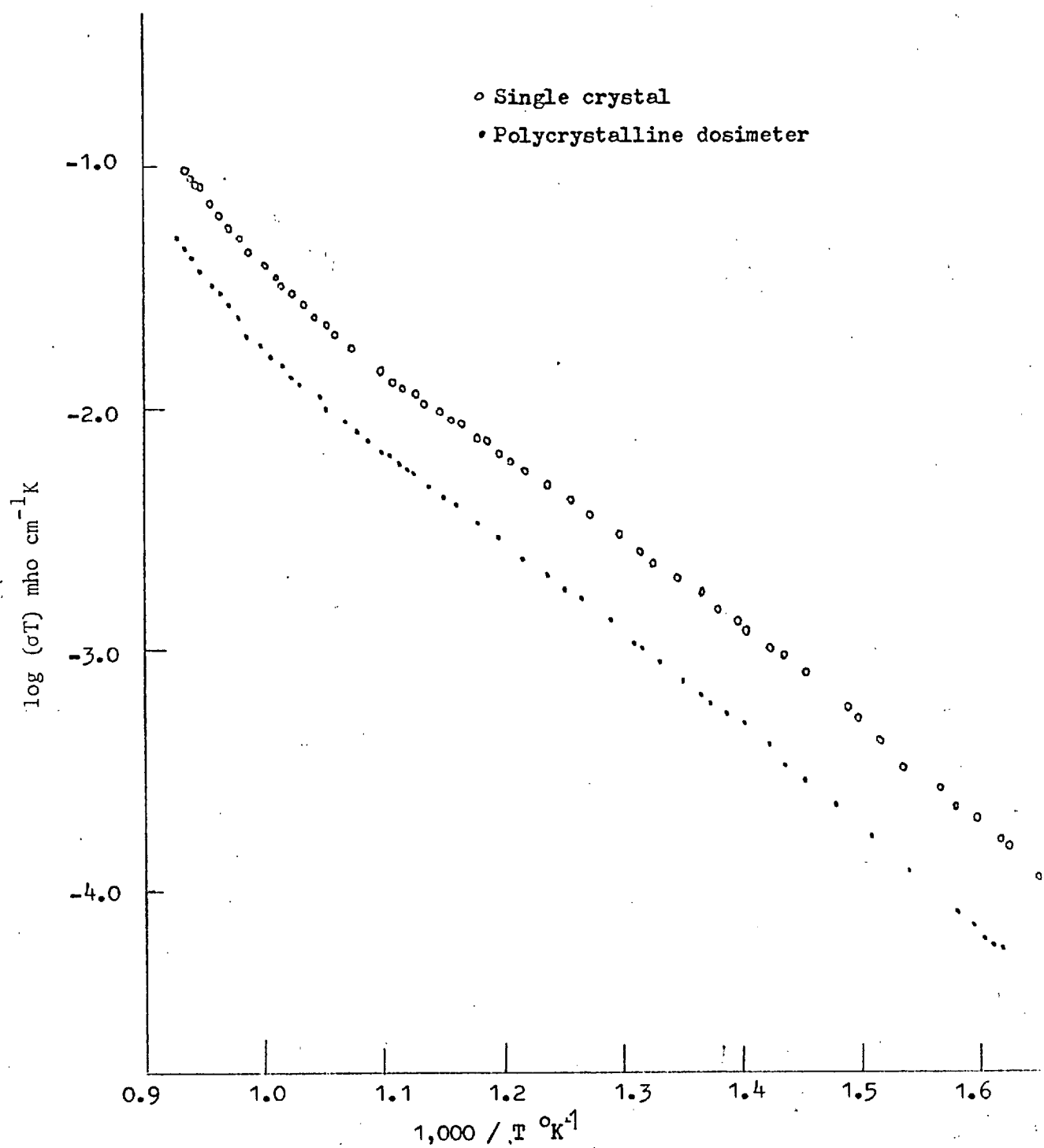


Fig.4.1(vii). Ionic Conductivity Plots for 400ppm Mg Material .

4.3. Microhardness

In order to try and establish whether the magnesium concentration affects the mechanical properties of the LiF microhardness values were obtained for single and polycrystalline specimens in both the normal and irradiated state. The results are summarised in Table 4.5. Preliminary results indicated that there was an apparent increase in the overall values for the polycrystalline material. The grain boundaries might act as obstacles to dislocation movement and hence cause an increase in the hardness; however, the size of the indentation compared to that of the particle size would tend to negate this explanation. Specimens prepared from LiF that had been finely ground prior to pressing were also examined (Table 4.5 (ii), (iv)) to try and establish some correlation between particle size and impurity level:

The effect of magnesium can most easily be seen by examination of the single crystals, where the effects of grain boundaries need not be considered. Table 4.5(v) shows a definite increase in hardness as magnesium concentration is increased. Hence it can be assumed that the magnesium impurity does act as a barrier to dislocation movement, a result that is in agreement with previous workers in the field (100).

The particle size effect must be carefully considered. Comparing Table 4.5(i) and (ii) it would seem that the finer ground material overall gives larger microhardness values, as might have been anticipated. The effect of the magnesium impurity on these specimens is not so obvious. There seems to exist an apparent fluctuation in values, there being no overall trend noticeable, compared to those shown in the single crystals. If grain boundaries cause an increase in microhardness and magnesium content also causes an increase then one might expect that the combined effect would yield noticeably increased values. Comparing the individual concentrations, *i.e.* each dopant level, this does in fact occur, although an overall view of each category, *i.e.* normal, fine ground and single,

obscures this result.

On irradiation there is a definite increase in the value of the microhardness. This can be attributed to two things; (i) an increase in the number of obstacles; (ii) an increase in the efficiency of the obstacles present.

Urosovskaya and Knab (101) have pointed out that although micro and macro methods of evaluation of the binding energy of dislocations in LiF give good agreement, the stress of activationless breaking differs by approximately an order of magnitude; hence great care must be taken when evaluating micro and macro characteristics. It would seem feasible that an increase in the density of obstacles should occur due to radiation damage in the ionic lattice, the main resistance to dislocations being clusters of point defects. In the LiF-Mg system the magnesium is known to exist as an impurity-vacancy complex.

Hayes and Nichols (102) have proposed a model, Figure 4.2. for the destruction of this vacancy-impurity complex under irradiation with the result of the formation of an interstitial halogen ion. If this is so then the F_2 resulting interstitial molecule would also act as a barrier to dislocation movement. Urosovskaya and Knab (101) have shown that this is in fact true, the F_2^- molecule being a stronger barrier than the isomorphous Mg^{2+} and cationic vacancy.

If the aggregates of Mg^{2+} -vacancy were dispersed, *i.e.* increase in concentration of possible barriers, then for increased magnesium concentration one would expect an increase in hardening, as is shown. However, one would also expect there to be an increase in hardening for increased magnesium if the efficiency of the system were increased. Hence no definite conclusion can be reached. It should, however, be pointed out that the lower concentrations increased in their hardness values by a greater percentage than the higher magnesium concentrations.

TABLE 4.5. Microhardness Measurements in Kp/mm^2 .

Dosimeters made from normal powders

(i)	Unirradiated	(ii)	Irradiated
Ref.	22.33		22.80
50	24.49		27.20
100	22.47		26.70
200	22.20		26.20
400	21.48		25.31

Dosimeters made from fine ground powders.

(iii)	Unirradiated	(iv)	Irradiated
Ref.	25.41		31.63
50	26.67		25.16
100	29.34		25.49
200	26.21		23.99
400	20.20		24.42

Single Crystals.

(v)	Unirradiated	(vi)	Irradiated
Ref.	18.41		18.35
50	17.96		19.28
100	18.54		19.48
200	19.28		19.82
400	19.41		20.10

A load of 10 gm was applied and readings taken visually from indentations made on the free surface of the pellet. Multiple measurements of each indentation were made and each disc was examined at five different places. Two indentations were made at these places. This gave an overall average result from 10 indentations. The accuracy of the measurements is $\pm 0.05 \text{ Kp/mm}^2$.

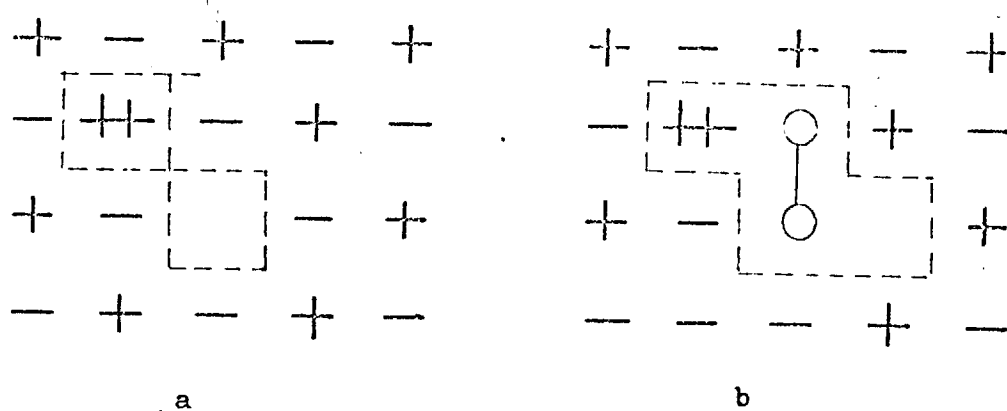
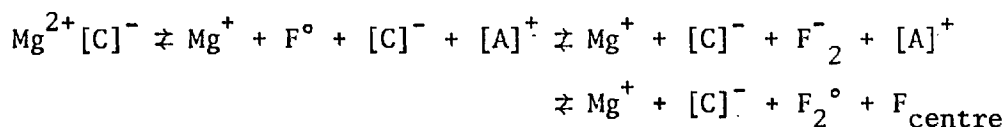


Fig.4.2. Formation of interstitial molecular halogen
as a result of radiation.

(Hayes & Nichols(102))

This would seem to give agreement to the probability that the lower magnesium is present as Mg^{2+} -vacancy dipoles which are destroyed on irradiation according to the formula postulated by Crawford and Nelson (103).



Since the F_2^{-} is a stronger barrier to dislocation movement an increase in hardness can be expected. For the higher concentrations, where aggregation is thought to occur the increase in efficiency would be masked by the hardening already produced by the large quantity of magnesium already present.

CHAPTER 5

Glow Curve Analysis

In order to isolate the plausible mechanisms involved several different aspects of the behaviour of the system were investigated.

- (i) The effect of the form of the material.
- (ii) The effect of the magnesium concentration.
- (iii) The effect of the quenching rate.
- (iv) The effect of repeated irradiations.
- (v) The effect of the annealing temperature.
- (vi) The effect of annealing time.

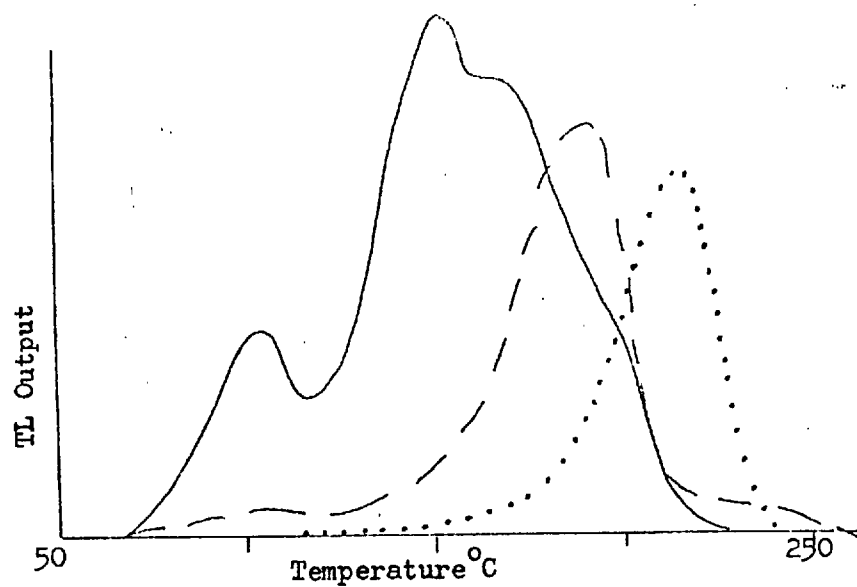
Of these the first two are the most fundamental to the system.

5.1. Effect of the Form of the Material

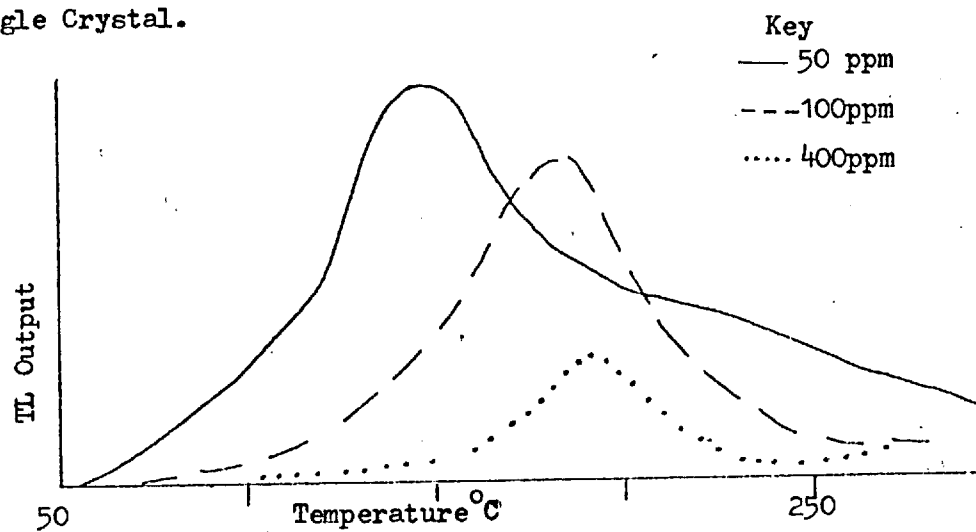
Figures 5.1(i), (ii) and (iii) show the effect of the form of the material for a range of compositions. All the specimens were irradiated in the as-grown condition. The low concentration of magnesium shows distinct low temperature peaks, these being at temperatures corresponding to peaks 2 and 3 ; whereas the higher concentrations show very little low temperature peak response, their main response occurring at peaks 4 and 5. With increasing magnesium concentration the response is shifted towards the high temperature range. (This will be discussed more fully in the following section.)

The form of the material is responsible for two major effects on the glow curves, namely a reduction in overall thermoluminescent response and a suppression of peak 5. On crushing the material the most noticeable effect is the drastic decrease in overall thermoluminescent response - the greater the amount of magnesium present, the larger the decrease. Coupled with this there is also a shifting of emphasis in the major peak display thermoluminescent response.

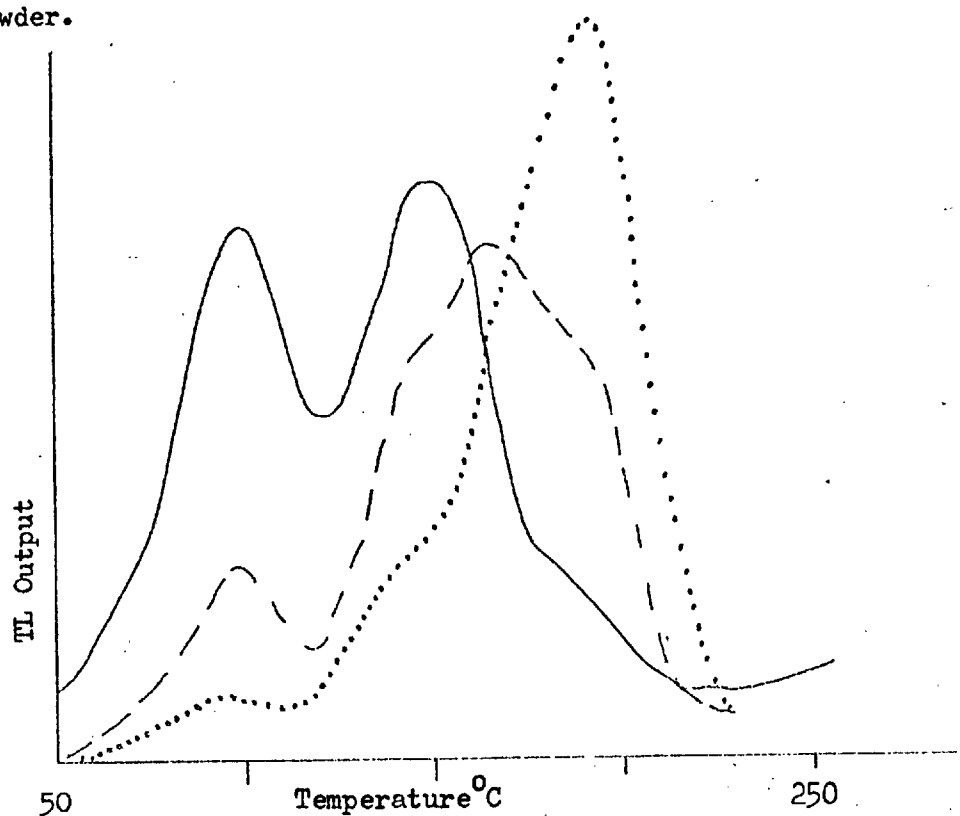
In the 50 ppm the single crystal shows distinct 2(150°C) and 3(180°C) peaks plus a possible extra peak occurring around 160°C. On crushing



(i) Single Crystal.



(ii) Powder.



(iii) Dosimeter.

Fig.5.1.

however, the resultant glow curve is a large peak 2, of diminished intensity. The pressed powder dosimeter displays increased sensitivity and a restoration of the initial peaks. Similarly in the 100 ppm sample only the major thermoluminescent centre peak is displayed for the crushed specimen, although the dosimeter exhibits characteristic curves similar to those of the single crystal. A slightly different result is obtained in the 400 ppm sample in that the single crystal exhibits an almost total thermoluminescent response at a temperature corresponding to peak 5 (210°C) which is 'shifted' to peak 4 (180°C) on crushing and remains even after pressing.

It would seem that the act of crushing the crystals and thus causing dislocations also causes a reduction or inhibition to the centres response for thermoluminescence. Since annealing is sufficient to reinstate the thermoluminescent response, (see Section 5.3), it would seem that inhibition rather than negation is caused by crushing the material. This would seem to be confirmed by the restoration and in some cases increased sensitivity of the material in the dosimetric form. The elimination of peak 5 by heavy plastic deformation is in agreement with the results reported by Petralia and Gnani (90) and by Srinivasan and De Werd (91). Although in both cases their deformation was much gentler they showed that peak 5 is reduced and in some cases a corresponding increase in the low temperature peaks occurs. It has already been pointed out (see Chapter 3) that peaks 4 and 5 are probably intimately related in that similar defects are the cause of the thermoluminescent centre. The results obtained from Figure 5.1 indicate that the defects responsible for the peak 5 are well-arranged clusters of Mg impurity-vacancy dipoles, which would be destroyed by the action of interpenetrating slip-planes, and those responsible for peak 4 are a looser binding of dipole clusters such as might occur by chance after crushing. The heat treatment afforded the material in production of the dosimeter is

sufficient to restore the sensitivity; in fact it is considerably increased, but not sufficient to restore the peak 5 response.

Peaks 2 and 3 are associated with the presence of free impurity-vacancy dipoles in the lattice. If these dipoles retain their identity after deformation then the suppression of peak 5 might well lead to enhancement of peaks 2 and 3. Petralia and Gnani (90) reported such findings for their deformed material. The only evidence to substantiate these claims found in the present experiments is that in the dosimeter glow-curves there appears to be some low temperature thermoluminescent response, all be it very slight, in the higher magnesium concentrations, and a somewhat disproportionate increase in peak 2 sensitivity for the 50 ppm sample.

5.2. Effect of the Magnesium Concentration

The major effect of increasing the magnesium concentration, for all forms of the material, is to shift the emphasis of the thermoluminescent response from those of the low temperature peaks 2 and 3 to the high temperature peaks 4 and 5. Figures 5.2.(i) and (ii) show the results for air cooled and slow cooled specimens. In both cases the reference and 50 ppm curves exhibit two distinct peaks corresponding to peak 2(98°C) and peak 3(147°C). Increasing the magnesium concentration to 100ppm causes a small low temperature peak 2 response accompanied by large 'compound' peak with a maximum at 160°C. The slow cooled graph shows a low temperature bias whilst that of the air cooled favours the high temperature side. A further increase in the magnesium (200 ppm) results in a single main dosimetry peak corresponding to peak 4(180°C) and 400 ppm results in a single peak 5(200°C). The distinction between 4 and 5 is more pronounced in the air cooled specimen.

Since peaks 2 and 3 are associated with free impurity-vacancy dipoles it is reasonable to expect that in low magnesium concentrations there will be a higher proportion of these compared with clusters of dipoles

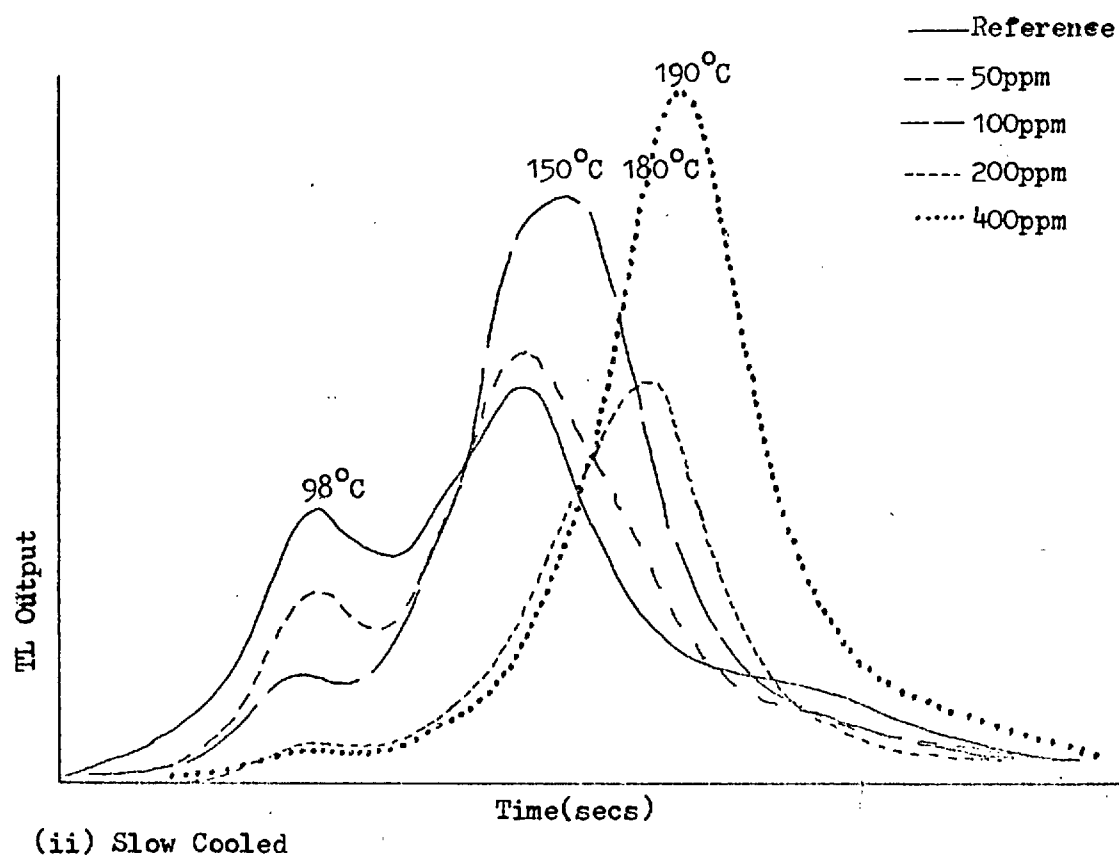
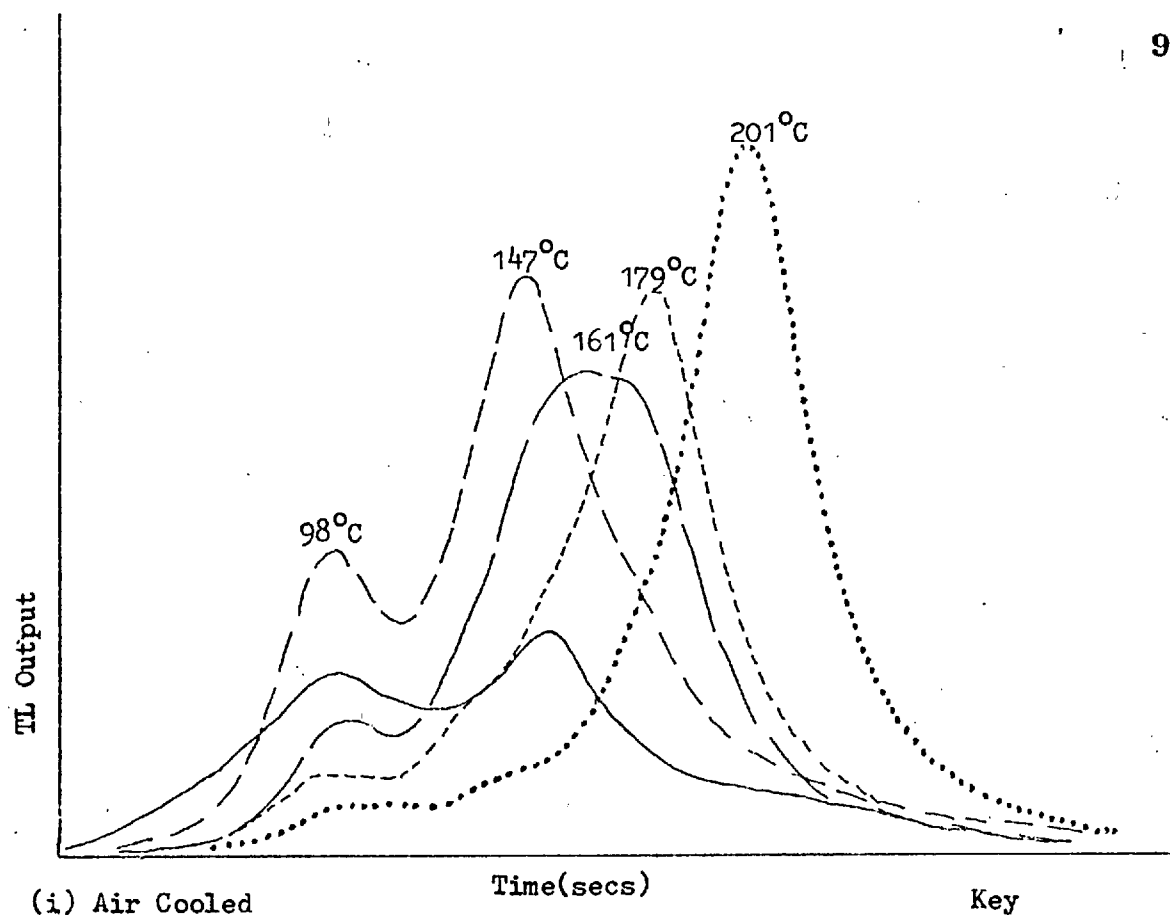


Fig.5.2.

in the form of dimers and trimers, hence low temperature peaks will predominate. On increasing the magnesium concentration the proportion of free dipoles present will be reduced and those present as clusters will form the majority, hence the high temperature response domination.

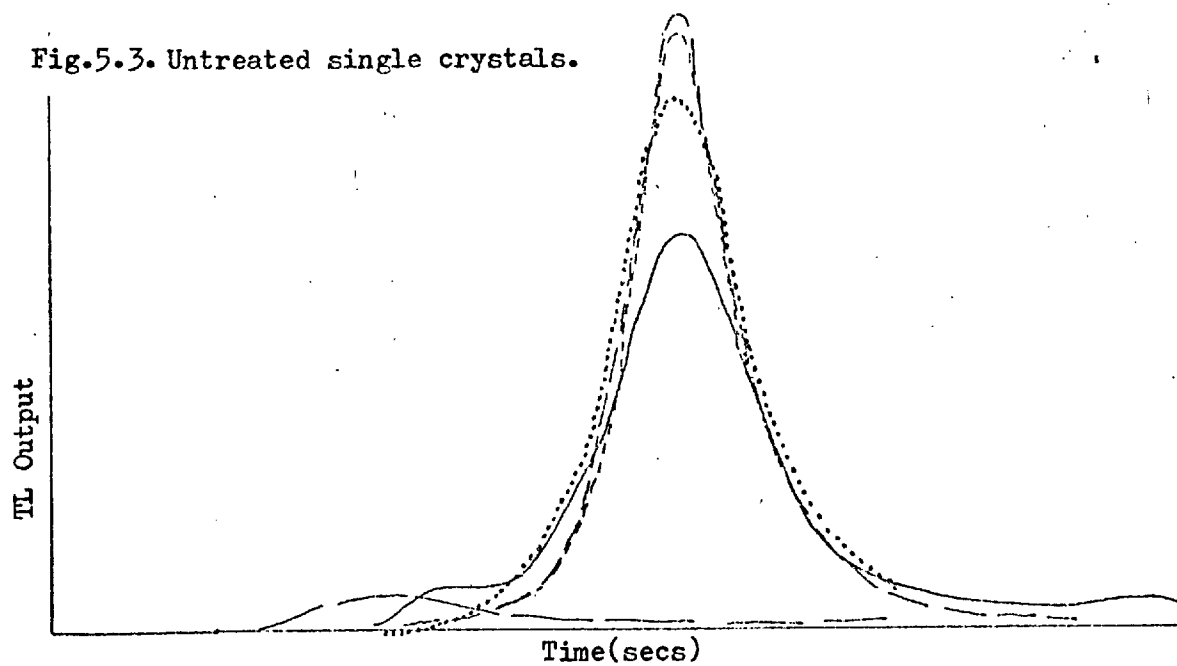
Figure 5.2. referred to specimens that had been annealed at 400°C prior to irradiation.

5.3. Effect of Repeated Irradiations

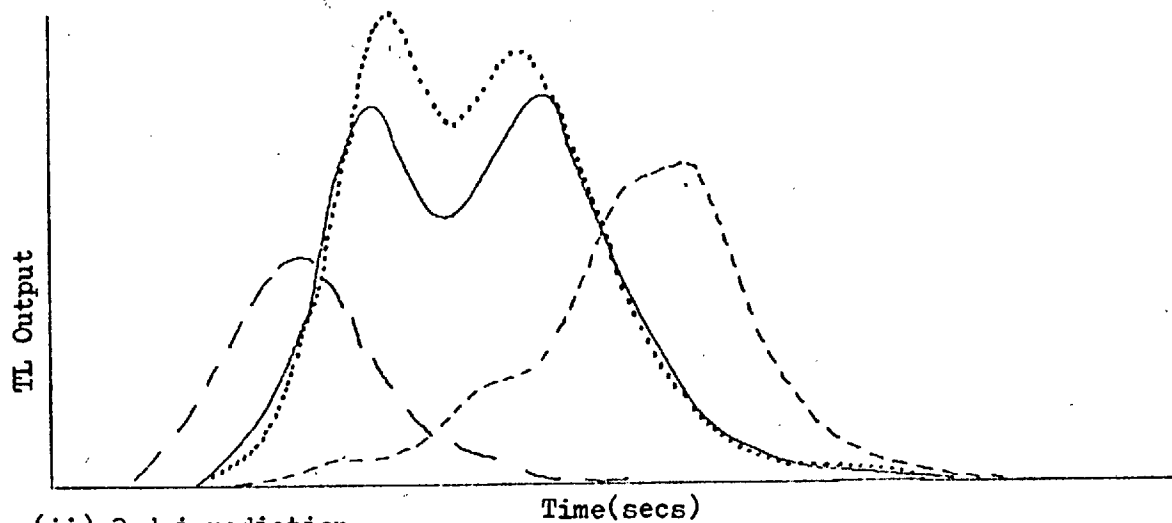
Figures 5.3.(i) and (ii) and (iii) show the effect of repeated irradiations on single untreated crystals. Figure 5.3(i) exhibits an apparent 'one-peak' phenomenon. All the specimens produce a single peak glow curve corresponding to peak 5(200°C) with an apparent increase in sensitivity with increasing magnesium concentration. On re-irradiating, however, this phenomenon is destroyed and 5.3(ii) results. The results obtained from 5.3(ii) are in agreement with those expected and obtained previously. (See section 5.1 and 5.2) Further irradiation 5.3(iii) causes an enhancement of the low temperature peak 2 in the lower magnesium concentration and a more definitive peak 5 in the higher concentration.

Why all the single crystal concentrations should exhibit a single dosimetric peak is puzzling. Its occurrence at peak 5 would be in agreement with ordered clusters, the material having undergone a long anneal and slow cool during fabrication (see Chapter 3.). Wintersgill, Townsend and Cusso-Perez (104) have reported that if crystals were exposed to room light between consecutive irradiations and glow-curve measurement the glow curves were not consistent. If, however, the crystals were kept in the dark between runs then the curves were reproducible, but differed slightly from the initial glow curve. Although they do not specify how different the curves were, it would seem to indicate that exposure to room light can interfere with dosimetric results. In the experimental procedures enforced in the present work the specimens were initially exposed to light, irradiated in 'A' cans,

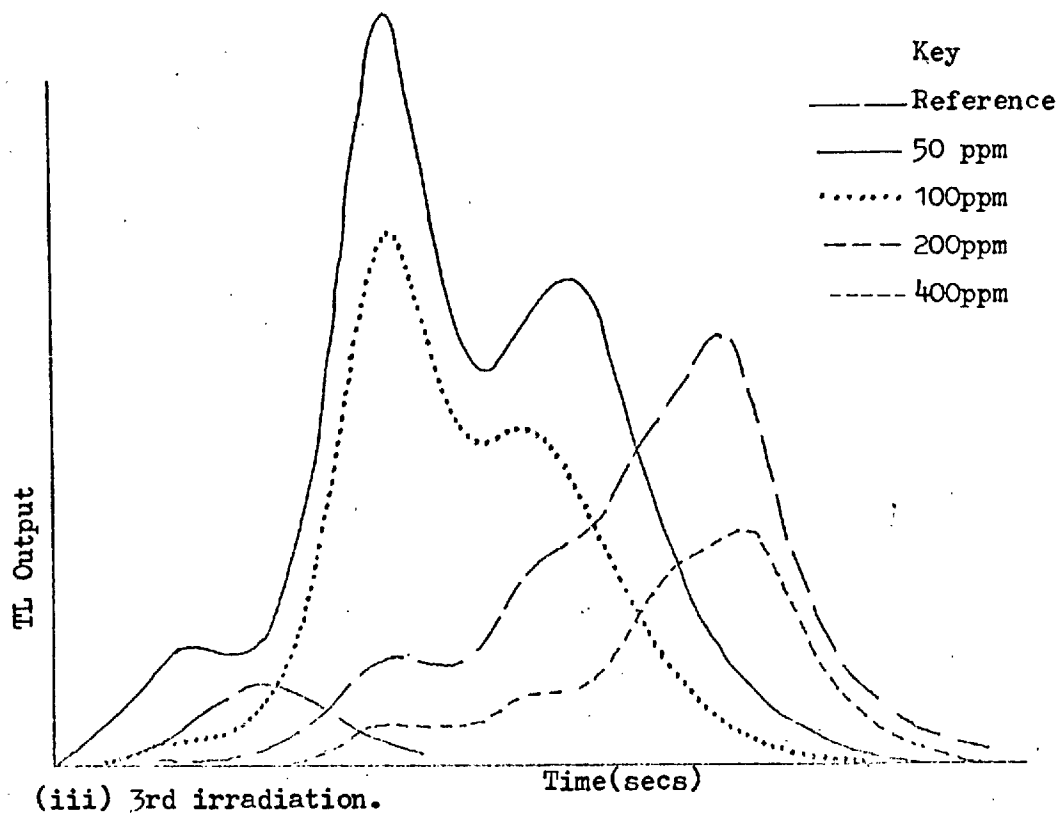
*This agrees with initial results obtained by NPL (see Fig. 2.12).



(i) 1st irradiation.

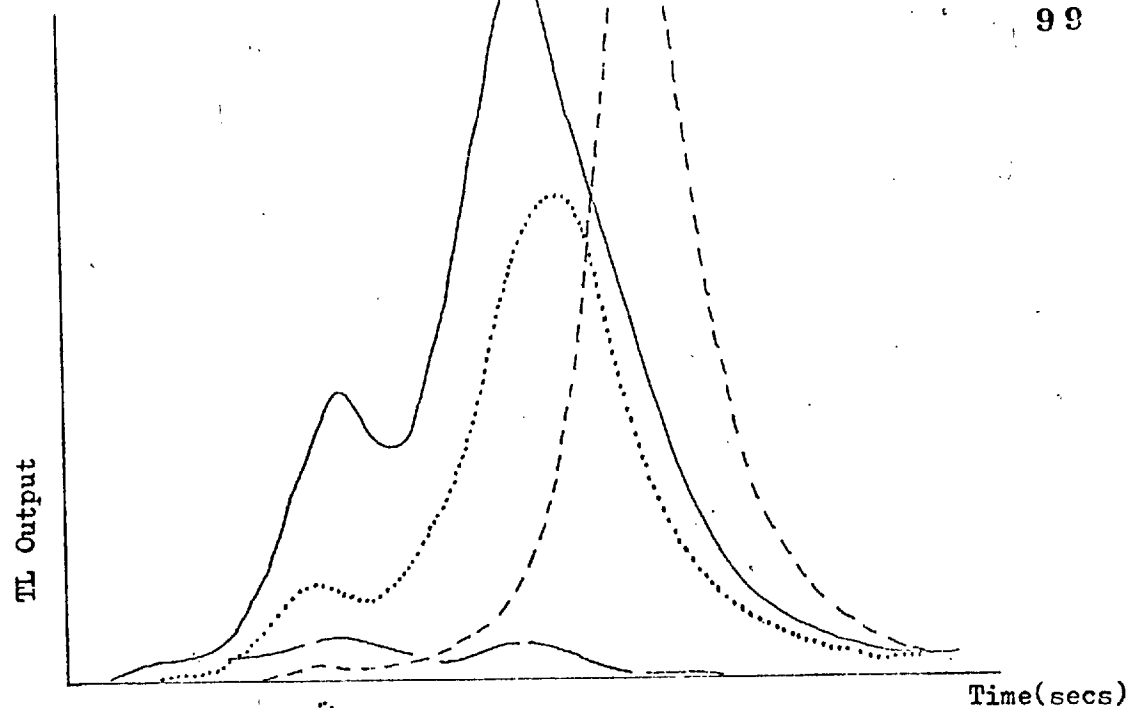


(ii) 2nd irradiation.

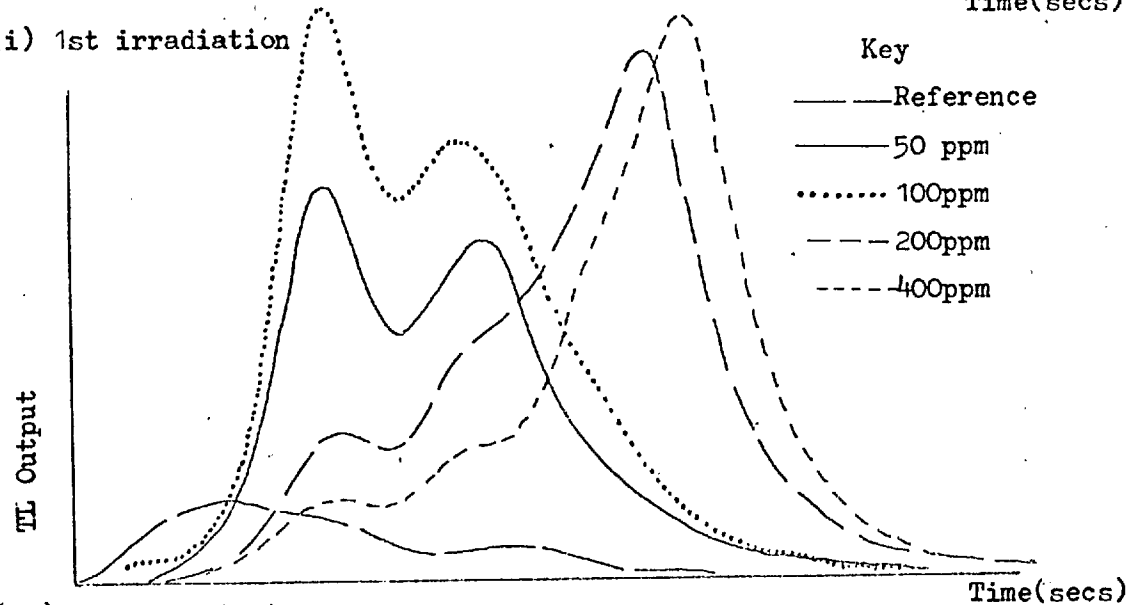


(iii) 3rd irradiation.

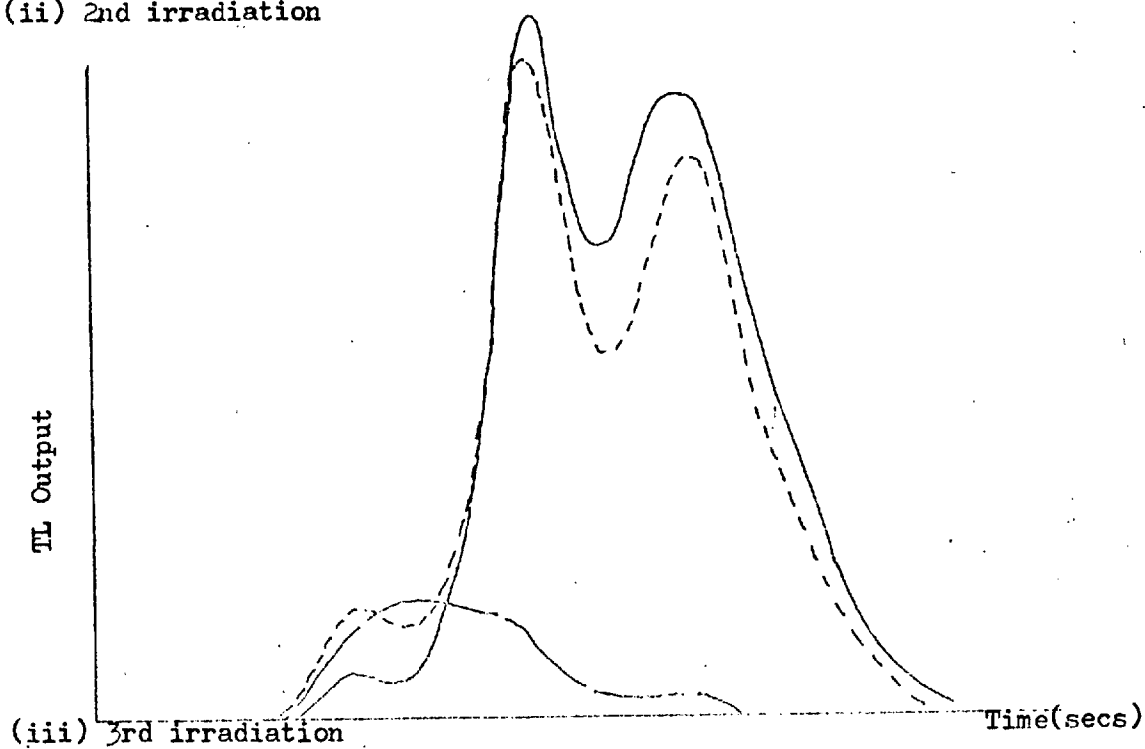
Fig.5.4. Slow Cooled single crystals.



(i) 1st irradiation



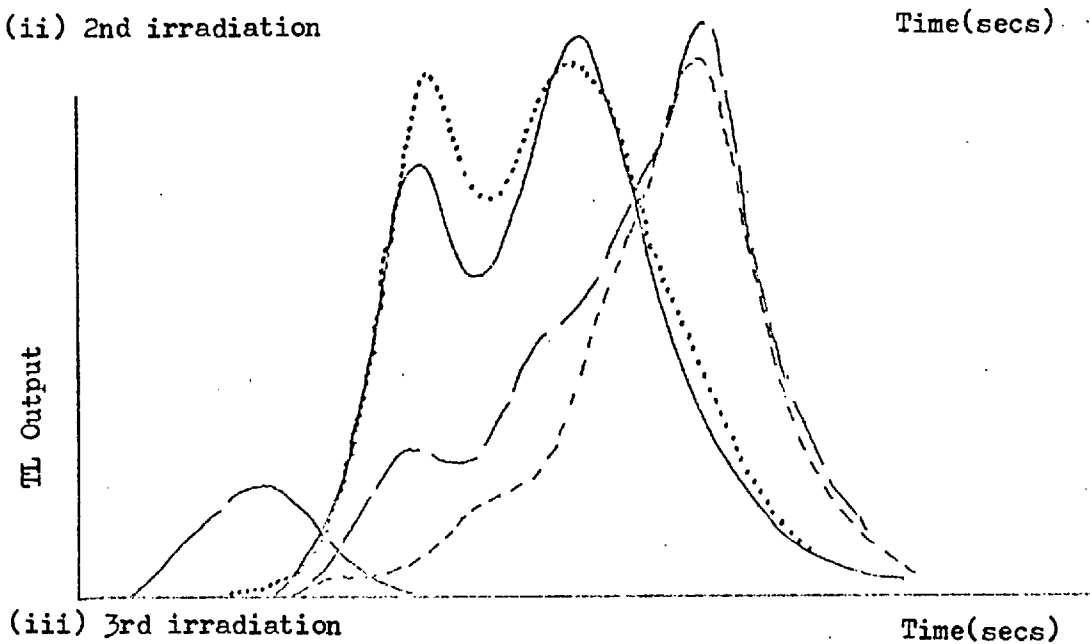
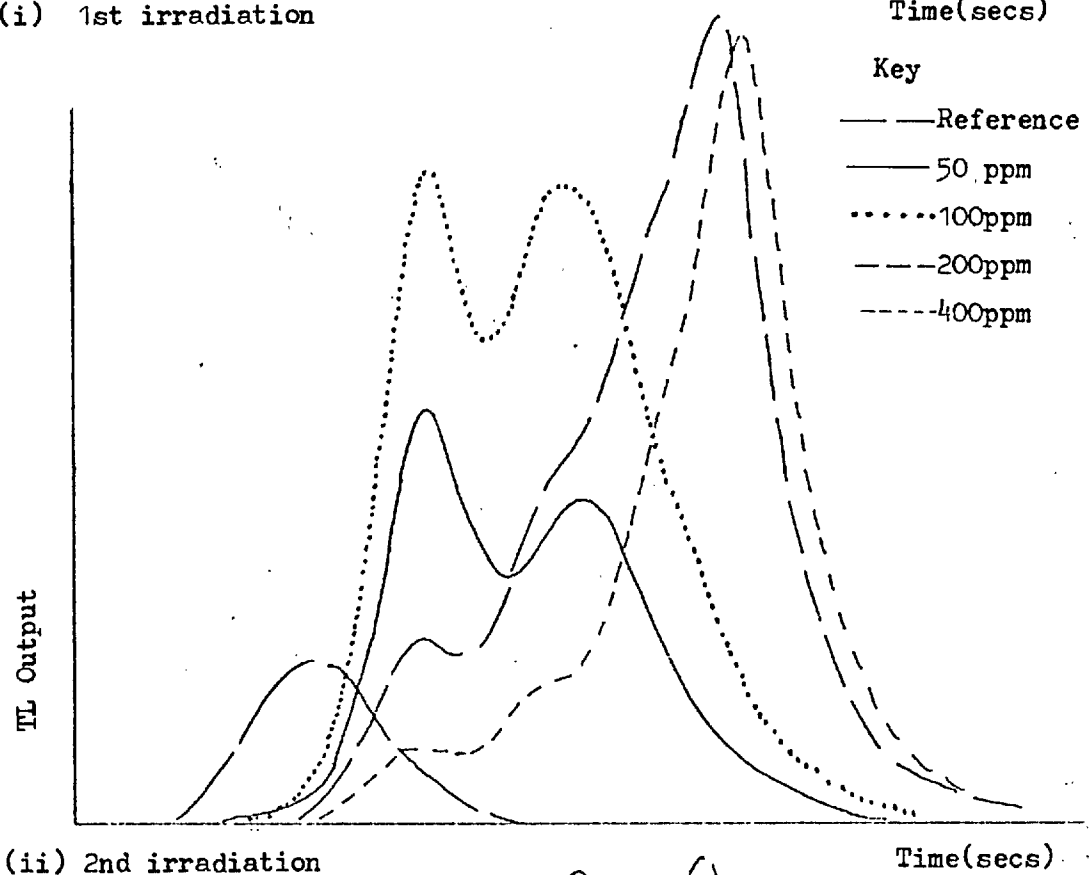
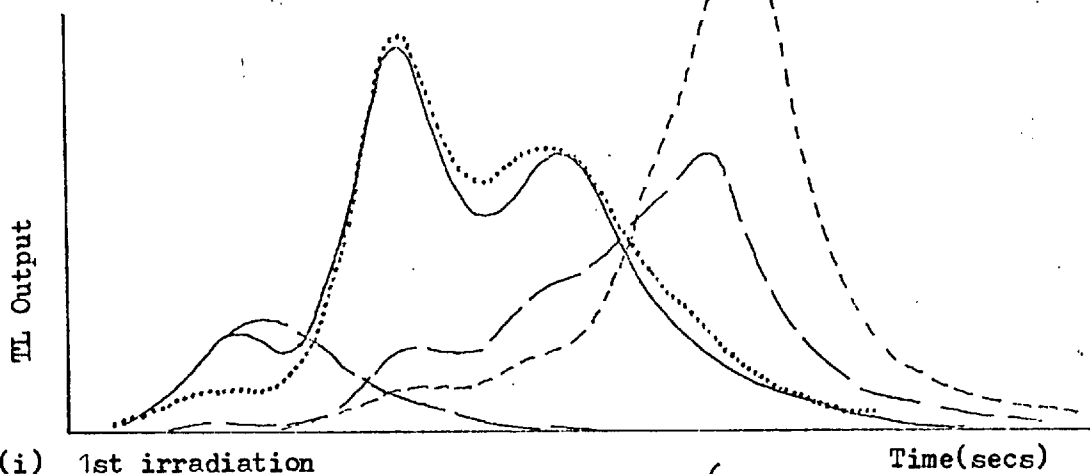
(ii) 2nd irradiation



(iii) 3rd irradiation

Fig.5.5. Air Cooled single crystals.

100



the relevant glow curve obtained, put back in the 'A' cans without prolonged exposure to room light and re-irradiated.

Figures 5.4(i) and (ii) and (iii) show repeated irradiations for slow cooled single crystals. The characteristic curves are obtained on first irradiation, *i.e.* there is no occurrence of the 'one-peak' phenomenon. This is to be expected if room light exposure plays a part in causing the effect since the specimens were immediately put into 'A' cans on completion of the heat-treatment and then irradiated. The main effect of re-irradiation is an enhancement to the sensitivity of the thermoluminescent response. This is especially noticeable in the 50 ppm and 100 ppm specimens where the main peak switches from that of peak 3 to peak 2 on re-irradiations. In the higher concentration, *i.e.* 400 ppm re-irradiation causes the main peak to move from peak 4 to peak 5, although the peak 5 obtained in all the specimens is at a slightly lower temperature 195°C than anticipated.

Figures 5.5(i), (ii), and (iii) show the results obtained from air cooled single crystals. Again the 'one-peak' phenomenon is missing. The repeated irradiations differ in the increased sensitivity of the low temperature peaks in the lower Mg concentrations. Initially peak 2 predominates but at the third irradiation peak 3 has taken over. This is the reverse of the effect on the slow cooled specimens.

5.4. Repeated Irradiations on Untreated Dosimeters

Figures 5.6(i), (ii), (iii), (iv) and (v) show the effects of repeated irradiations on untreated dosimeters. No 'one-peak' phenomenon exists for these untreated dosimeters. The reference dosimeter, Figure 5.6(i) initially comprises of two peaks, corresponding to peak 2 and peak 3. As repeated irradiations are made peak 3 is reduced in height and peak 2 increased. In extreme cases plateauing would seem to occur although this does not seem to be a permanent feature since on re-irradiation (5th time) a reduced definitive peak is again obtained.

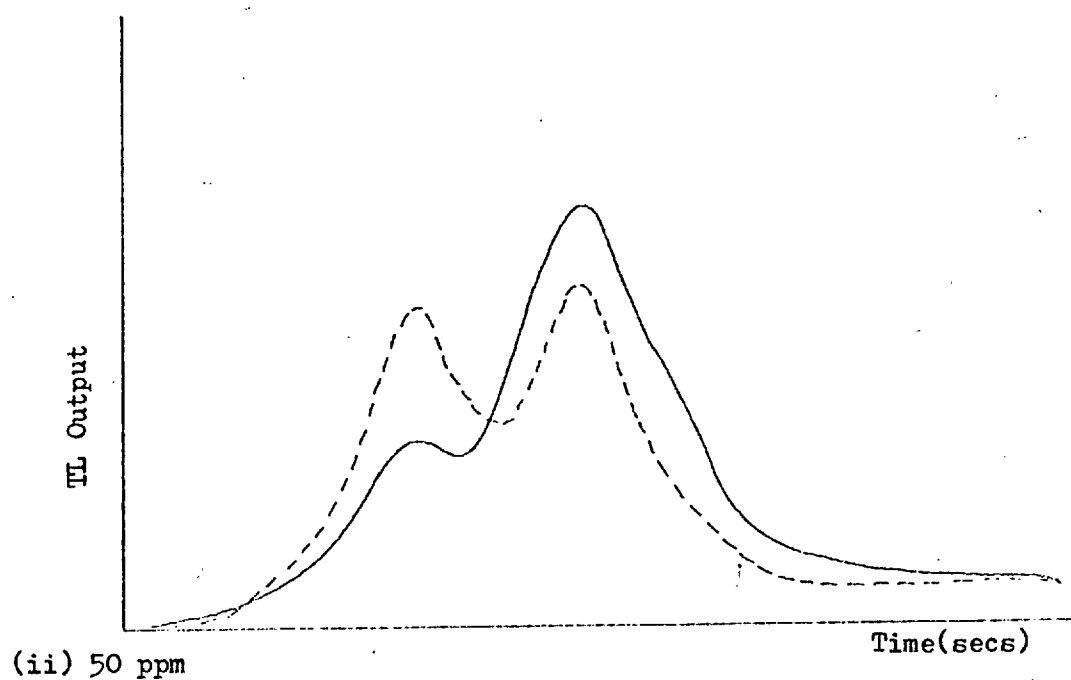
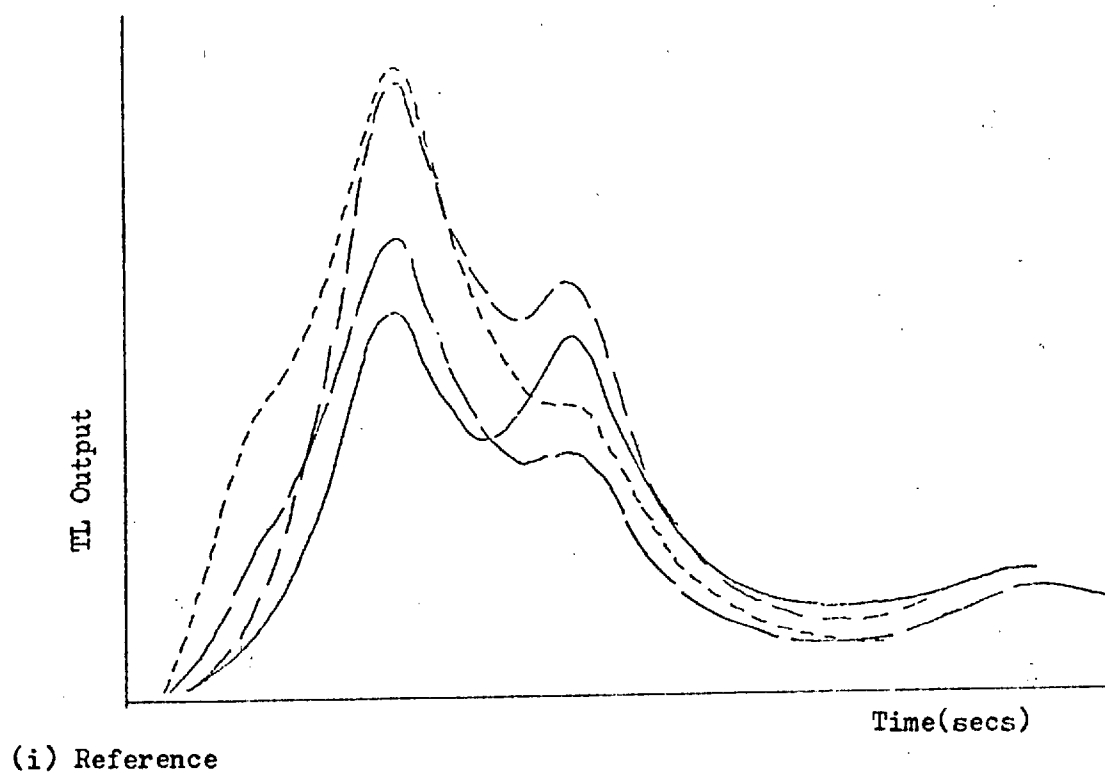
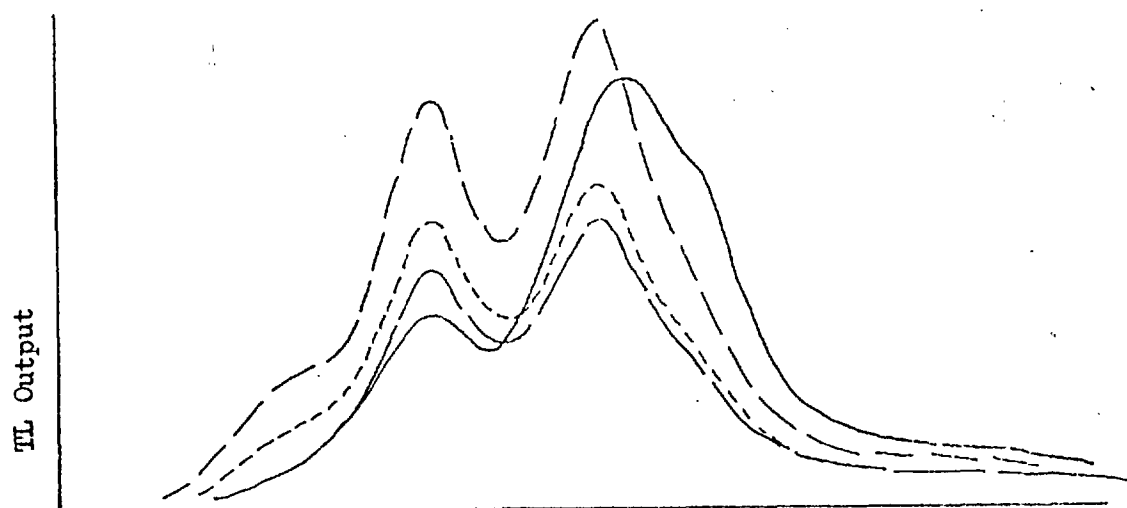
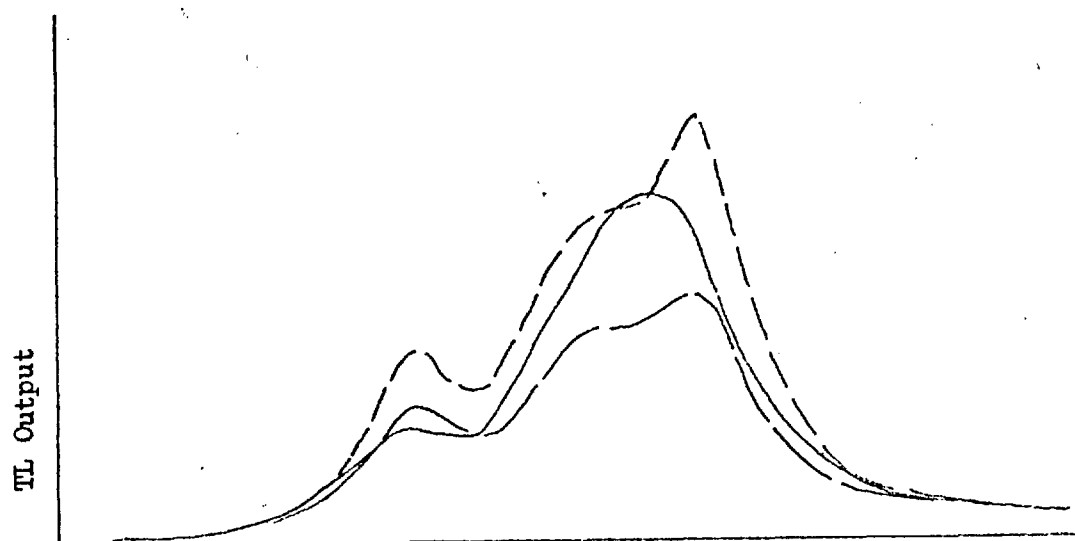


Fig.5.6. Repeated Irradiations on Untreated Dosimeters.



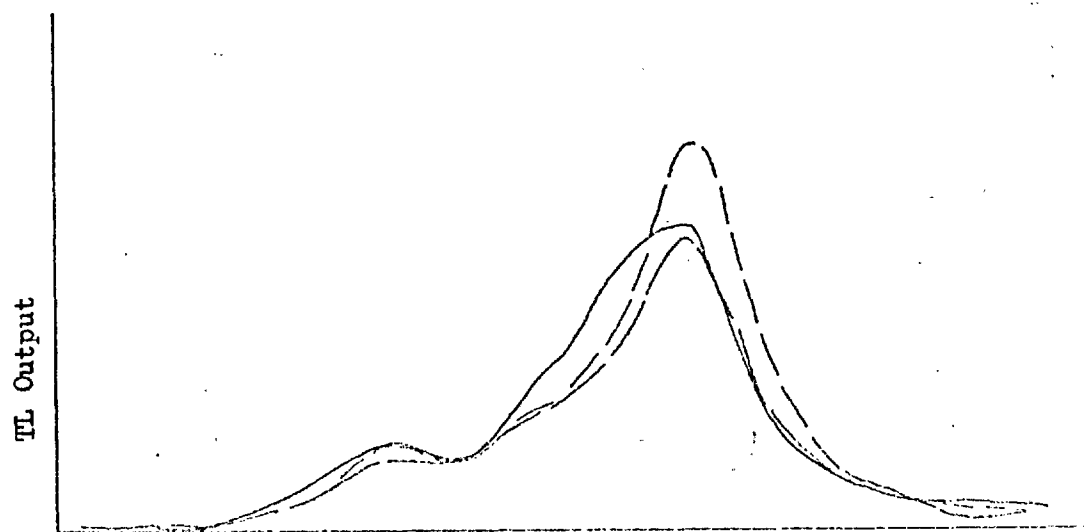
(iii) 100ppm

Time(secs)



(iv) 200ppm

Time(secs)



(v) 400ppm

Time(secs)

Throughout peak 2 remains dominant.

An increase in the magnesium concentration results in a two peak glow curve as predicted by previous results but it is peak 3 that is very much the predominant peak (Figure 5.6(ii)). On repeated irradiations the first peak is enhanced but it would seem that the growth of peak 2 does not expressively take place at the expense of peak 3, *i.e.* the increase in peak 2 is not due to a breakdown in the mechanism of formation of peak 3 defects. If this were the case then there should exist some relationship between the number of radiations and increase/decrease in peak heights. This is not so. The increase in sensitivity can be partially explained by the failure to 'read-out' all the thermoluminescent centres during each reading.

By the time we get to 100 ppm the magnesium concentration shift can be seen. Figure 5.6(iii) shows the results of repeated irradiations. The initial curve exhibits three main peaks. The first corresponding to peak 2, the second and third peaks comprising of a compound peak, (Compare this with Figure 5.1(iii)), with the major peak occurring at 160°C and a high temperature 'bump' corresponding to peak 4. On re-irradiation there is a change in the glow curve. The peak at 160°C (designated 3½) disappears and the resultant curves correspond to peaks 2 and 3, the second peak being slightly more predominant.

With even more magnesium addition, Figure 5.6(iv) the characteristic thermoluminescent dosimeter curve begins to emerge although the initial curve comprises of two distinct peaks. The first of these coincides with peak 2, the second is a 'compound curve' with no definite maximum. On re-irradiation this broad banded peak is resolved into two distinguishable maxima, the higher temperature peak corresponds to peak 5. Still further irradiations enhance this resolution, the second peak growing, possibly, at the expense of the first. The definition of the second and third peaks certainly improves.

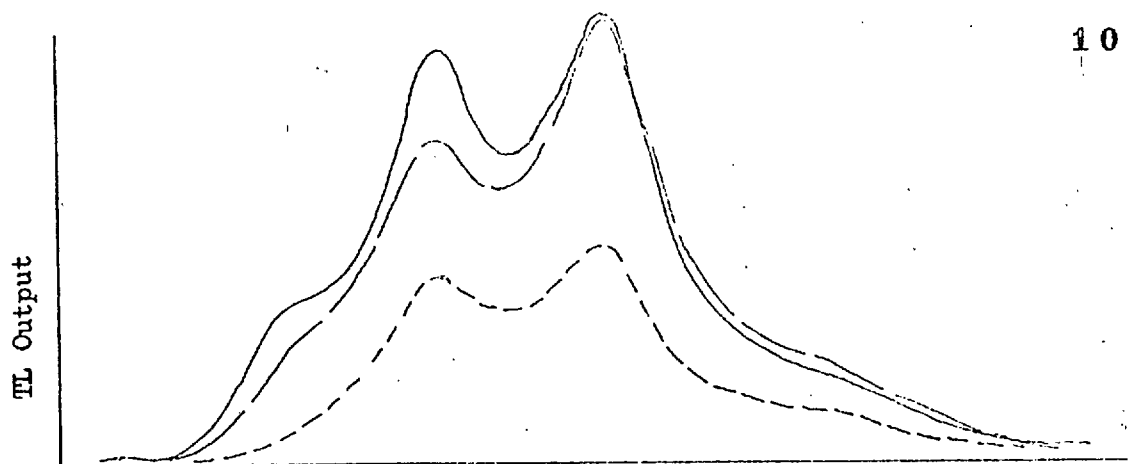
At very high magnesium concentration (400 ppm) the emphasis is again on the high temperature response, Figure 5.5(v). Initially two peaks are obtained, the second of these looks like a compound curve having two 'bumps' on the low temperature side of the maximum. These correspond to peaks 3 and 4 with the maximum occurring at peak 5. On re-irradiation this compound peak is resolved into one main peak corresponding to peak 5. Again sensitivity is increased by repeated irradiations.

5.5. Irradiation of Air Cooled and Furnace Cooled Dosimeters

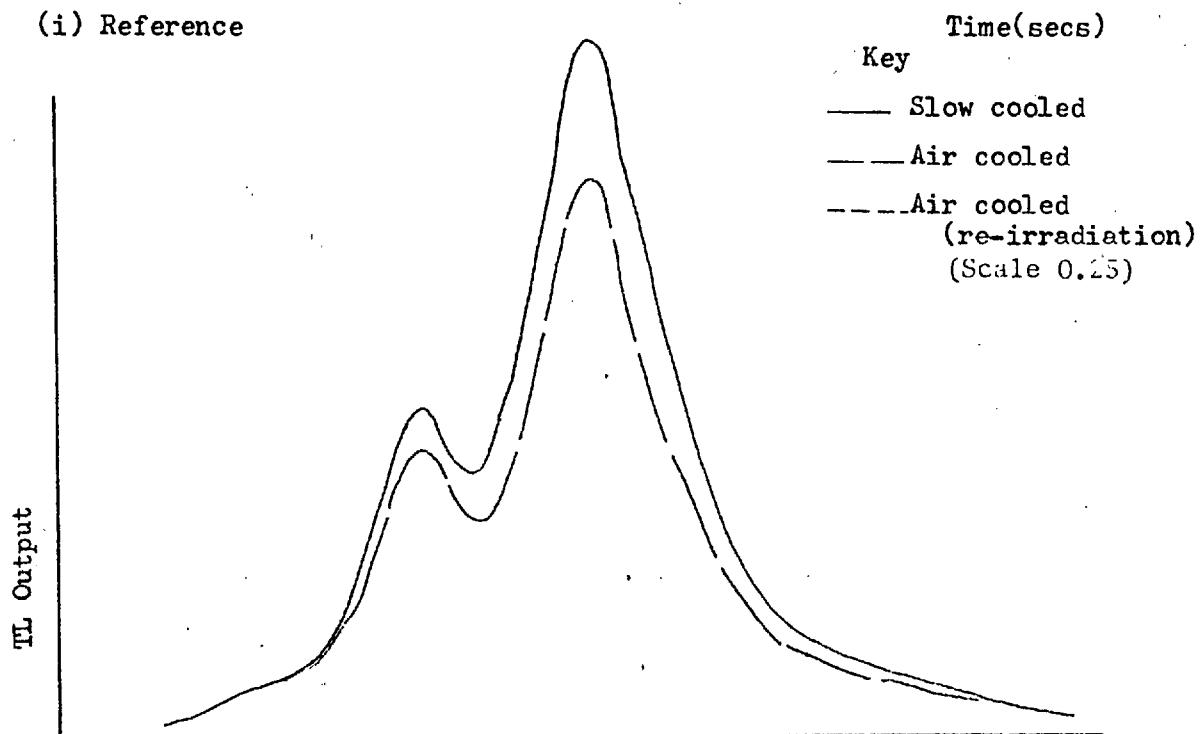
Figures 5.7(i)-(v) show the results of irradiations on heat treated dosimeters. Comparison of the curves has been made for each of the five dopant levels separately. The main difference between the air cooled and furnace cooled specimens in Figure 5.7(i), *i.e.* the reference dosimeter, is that of the relative heights of the peaks produced. These peaks correspond to peaks 2 and 3 respectively. Although the second of these peaks is the dominant it is more noticeable in the air cooled specimen. On re-irradiation, however, the air cooled specimen shows an increase in peak 2 sensitivity and the curve tends to that of the slow cooled. The apparent increase in peak 2 is in agreement with the results obtained from the untreated dosimeters. (Figure 5.6(i)).

The 50 ppm specimen (Figure 5.7(ii)) seems to be little affected by either the rate of cooling or re-irradiation.

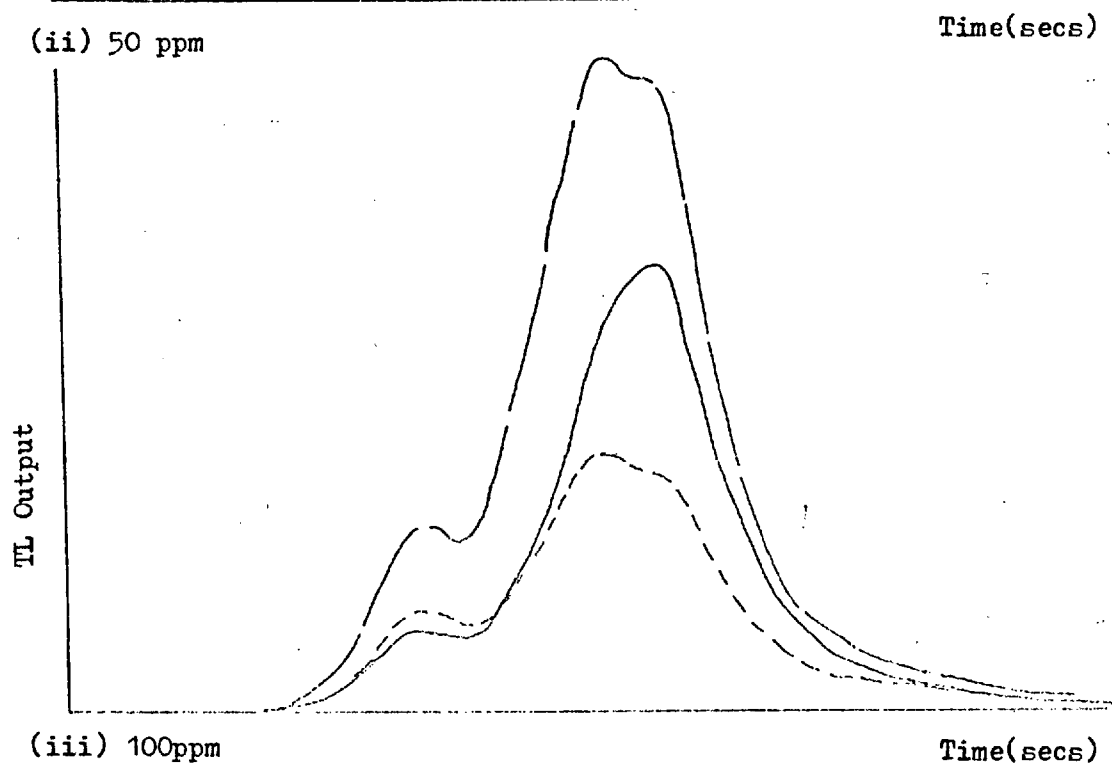
The further increase of magnesium to that of 100 ppm (Figure 5.7(iii)) shows the first real difference due to the cooling treatment. For the slow cooled specimen there are initially two peaks. The first corresponds to peak 2, as it does in the air cooled specimens. The second, however, is another compound curve with a decided bias towards the low temperature side. The maximum corresponds to peak 4 and the 'bump' to peak 3. The air cooled specimen on the other hand also has a 'compound-type' curve but the bias is on the high temperature side. The maxima in this case corresponding to peaks 3 and 4 respectively. Re-irradiation of the air



(i) Reference

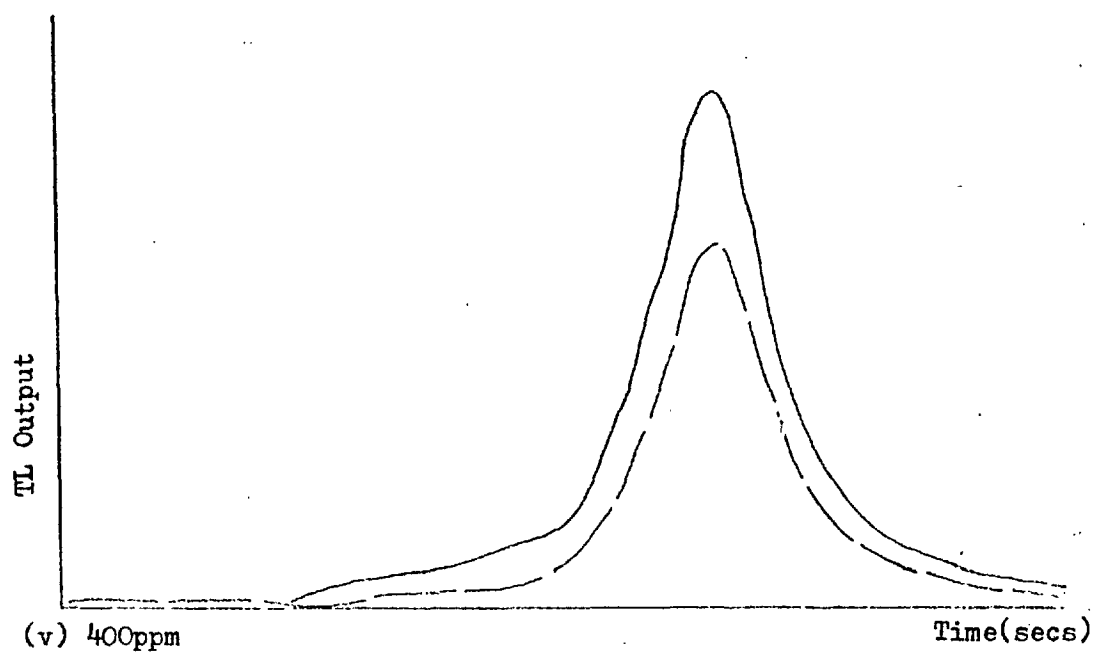
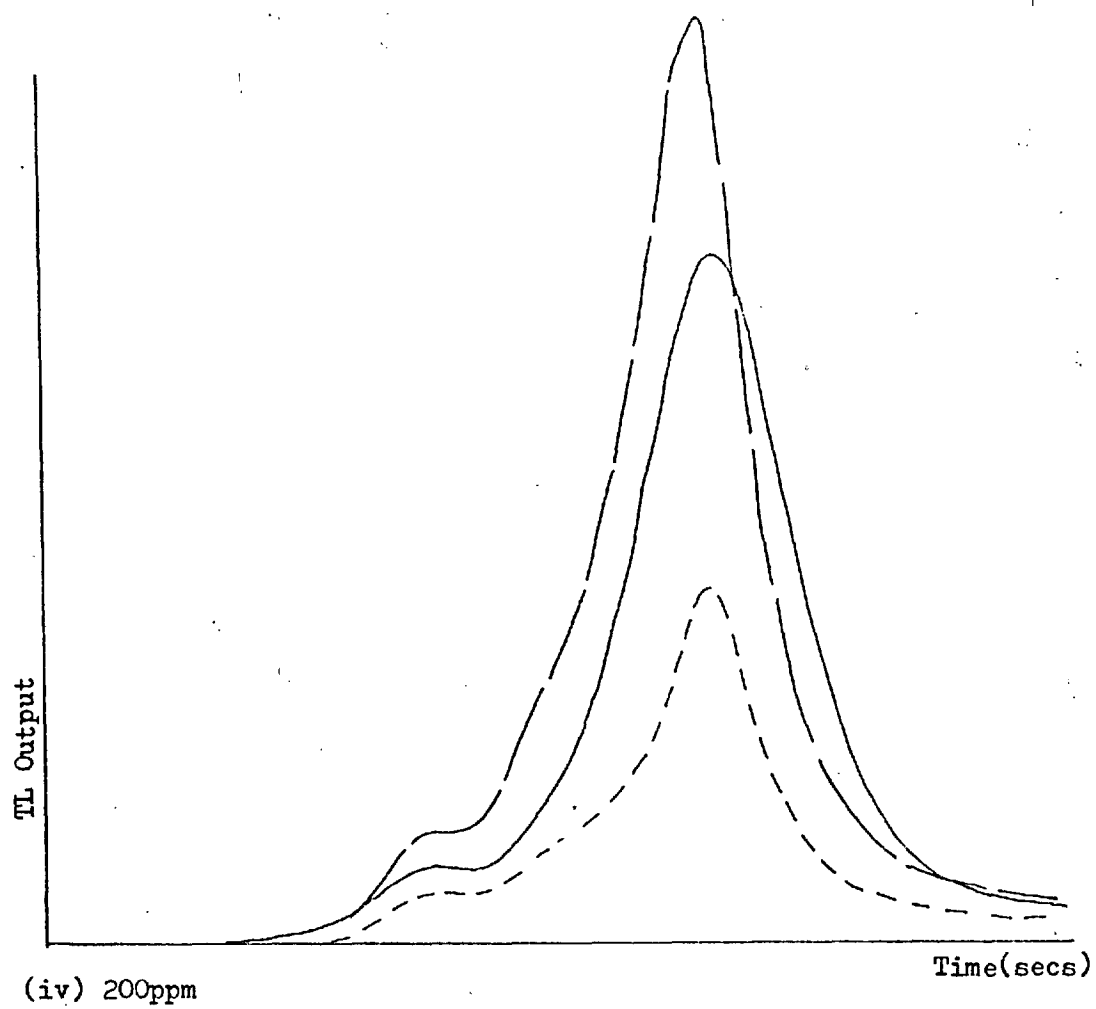


(ii) 50 ppm



(iii) 100ppm

Fig.5.7. Effect of Irradiation on Heat Treated Dosimeters.



cooled specimens increases the height of peak 2, the second peak remains the same in overall shape, *i.e.* the bias is towards the high temperature so that unlike the reference dosimeters (Figure 5.7(i)) repeated irradiations do not lead to a reversal to that of the slow cooled dosimeter.

For the 200 ppm (Figure 5.7 (iv)) specimens not much difference is exhibited between the differently heat treated specimens, a main peak 5 being obtained, although in the re-irradiated air cooled specimens better resolution is obtained so that a low temperature 'bump' appears.

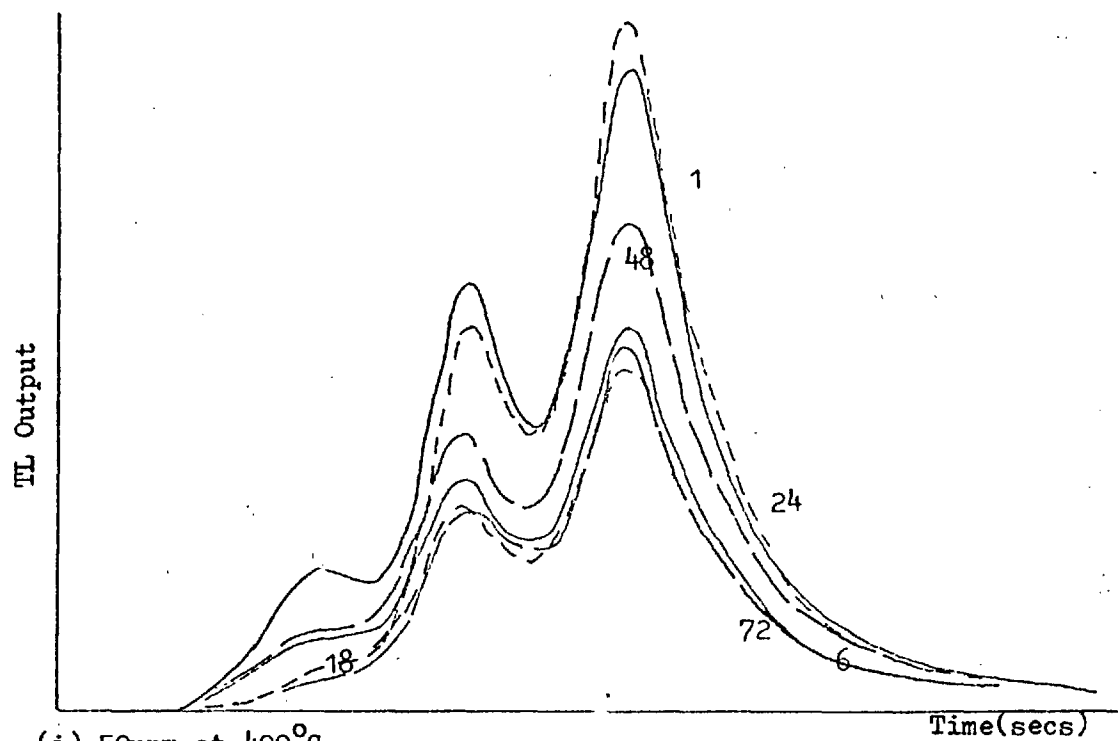
The 400 ppm specimen (Fig. 5.7(v)) exhibits one main peak, corresponding to peak 5.

5.6. Effect of Time and Temperature

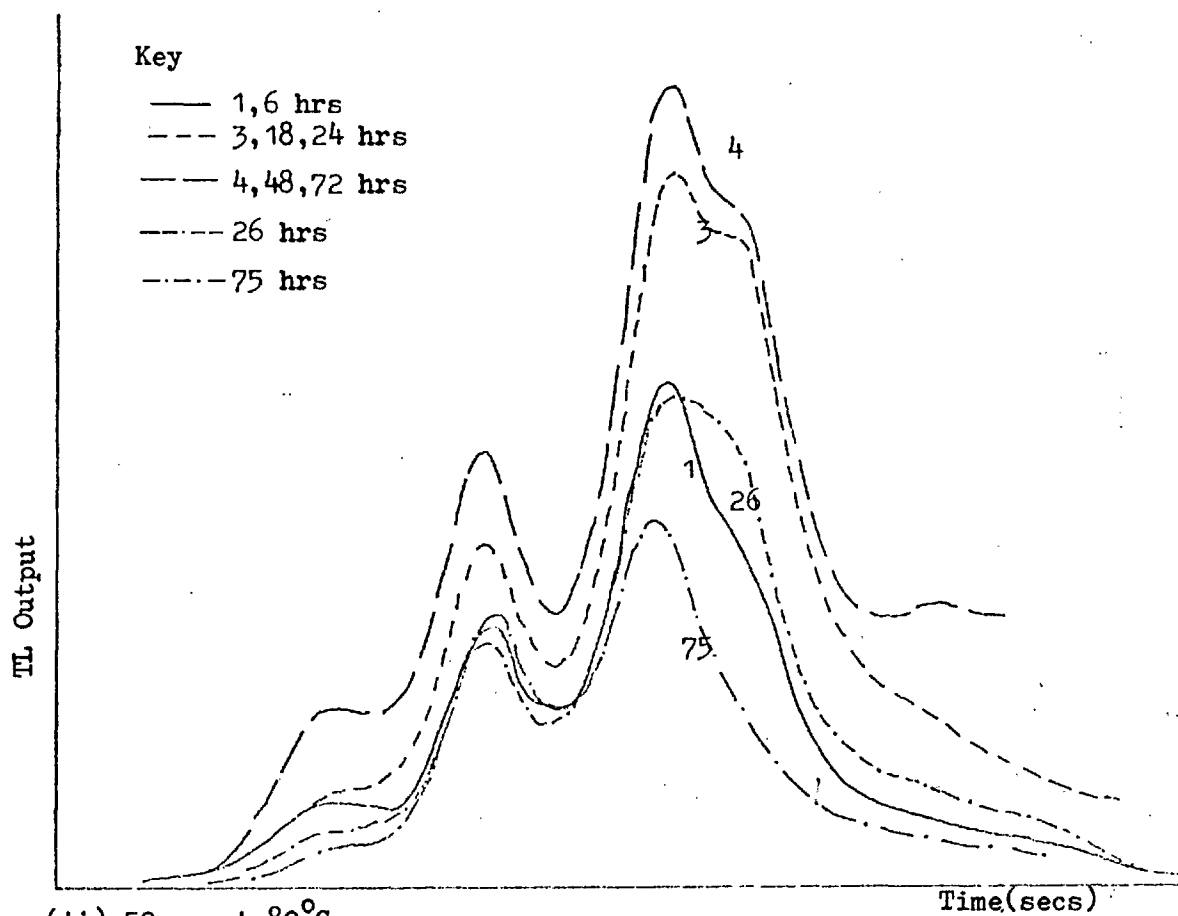
Since the two main stated temperatures for annealing treatments are those of 80°C and 400°C (see chapter 2) it was decided to examine the effect of time on dosimeters exposed to these temperatures. The 'standard' annealing treatment being 24 hours at 400°C followed by 80°C for one hour.

The results for 50 ppm are summarised in Figures 5.8(i) and (ii). From the graphs obtained here it would seem that the overall shape of the glow curve is independent of the time. Two main peaks are obtained corresponding to peak 2 and peak 3. Maximum sensitivity would seem to occur at 24 hours with a steady decrease as the annealing is prolonged.

For specimens exposed to the lower temperature (Figure 5.8(ii)) there is a definite change in the thermoluminescent response. Initially two main peaks exist, the first corresponding to peak 2, the second to peak 3, with a high temperature 'bump' occurring at a temperature corresponding to peak 4. This 'compound curve' becomes resolved if annealing is allowed to continue, reaching a maximum definition around 4 hours (Figure 5.8(iii)), thereafter the glow curve tends towards its original shape. It would seem to indicate that in order to obtain maximum resolution from the glow curves using 50 ppm dosimeters an anneal of

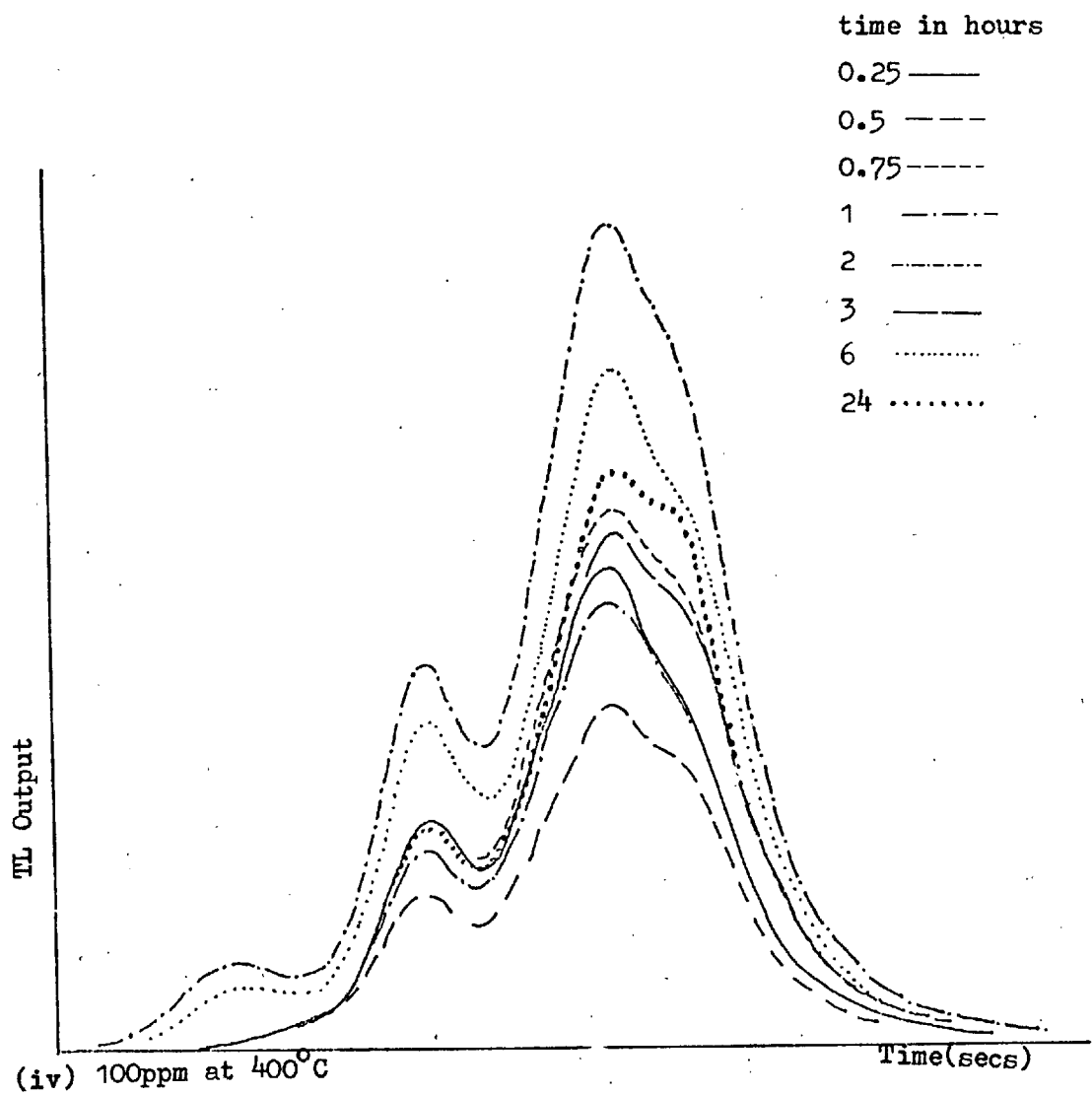
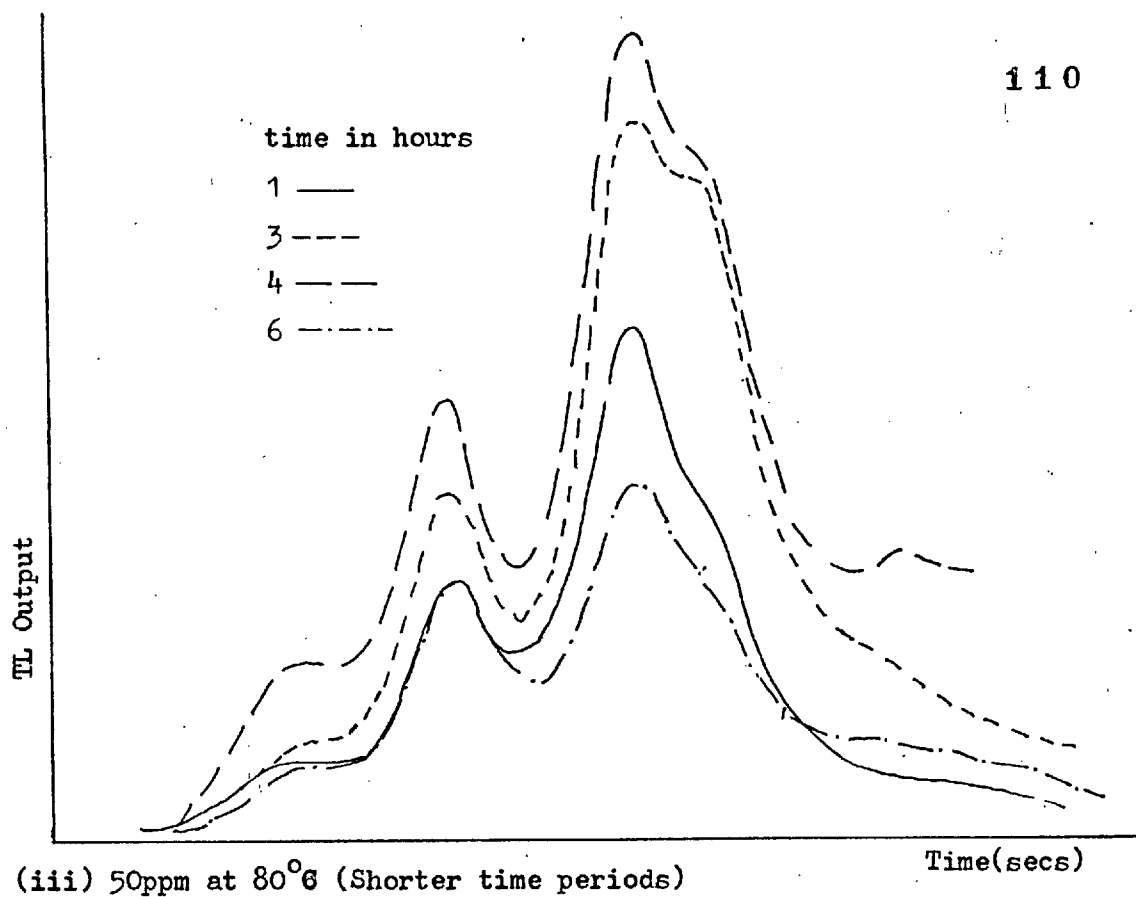


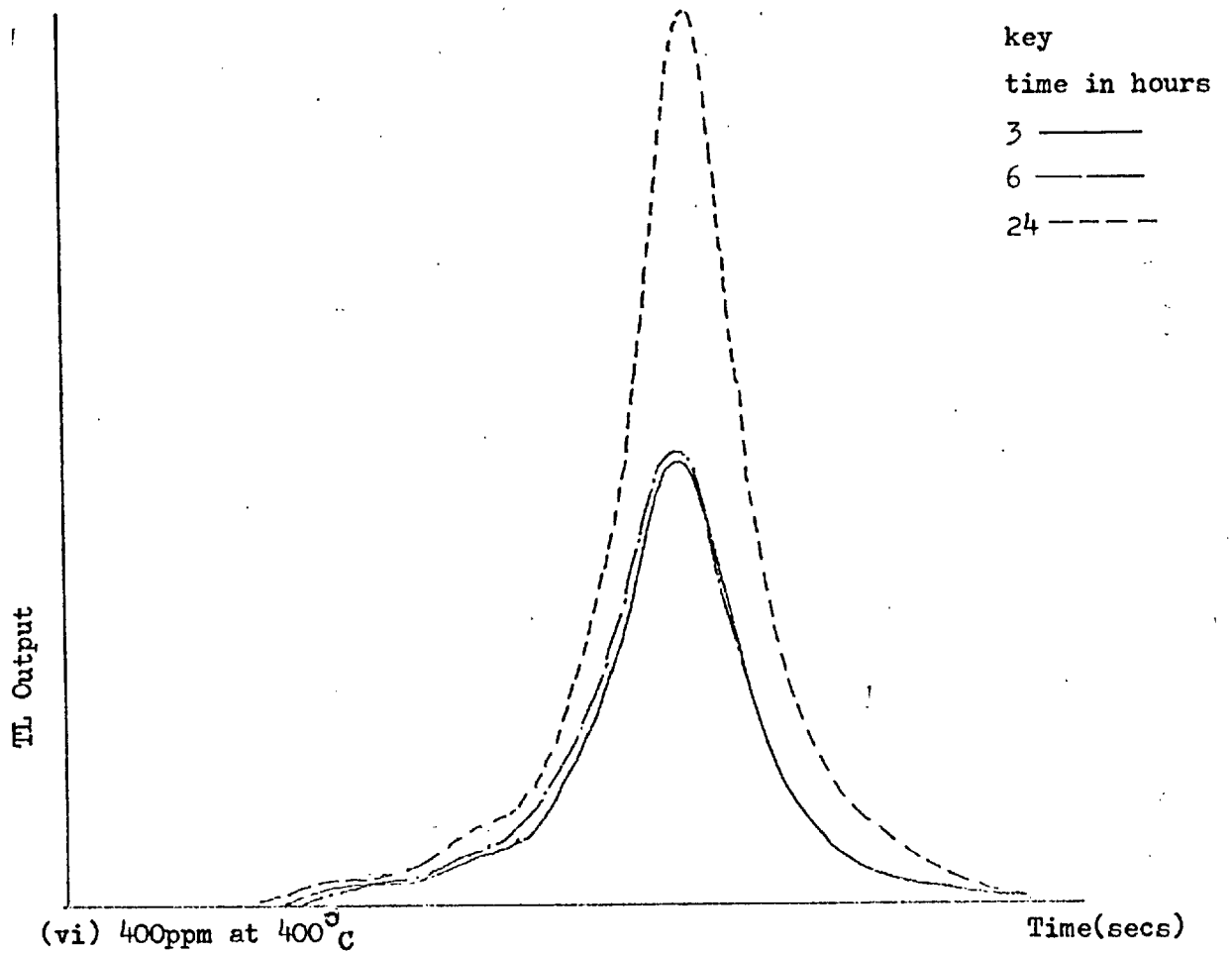
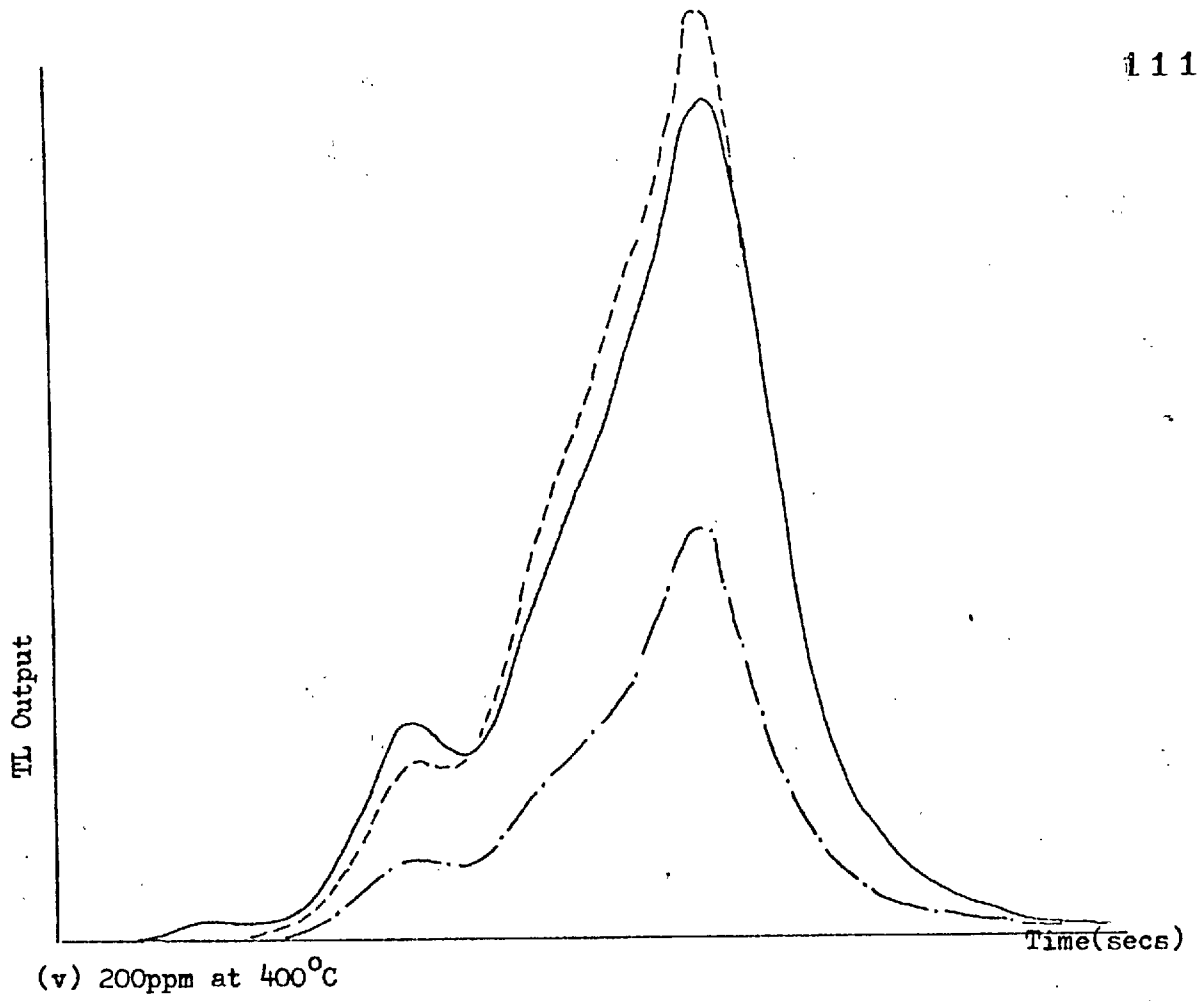
(i) 50ppm at 400°C



(ii) 50ppm at 80°C

Fig.5.8. Effect of Time and Temperature.





3-4 hours is preferable rather than the stated standard one hour used for TLD-100.

Repeated irradiation measurements were made on specimens which had been annealed for three hours. The results are summarised in Table 5.1. The peak distance refers to the distance between successive maxima, corresponding to peak 2 and 3. The peak heights are the ratio of vertical heights of these peaks. The effect of repeated irradiations is in fact negative in that neither the shape of the glow curve is altered nor is the sensitivity enhanced or decreased. The ratio of the peak heights increases slightly $0.6143 \rightarrow 0.6778 \rightarrow 0.6675$ but within the sphere of experimental error (15%) this is insignificant.

Thus it would seem that for practical dosimetry use a 50 ppm disc annealed at 80°C for three hours will give reproducible and calculatable results.

The 100 ppm dosimeter annealed at 400°C (Figure 5.8(iv)) exhibits its characteristic curve, (see Figure 5.1(iii)) with the low temperature peak corresponding to peak 2 and the maximum of the second peak occurring around 160°C with a 'bump' at peak 4 (180°C). As the annealing is allowed to continue this bump becomes more resolved.

Further increase in the dopant levels again produce the expected curves (Figures 5.8.(v) and (vi)). As might have been inferred from the previous results of 400°C anneals the basic characteristic curve is unaltered by prolonged exposure to the standard annealing temperature. Although all specimens received exactly the same radiation dosage the thermoluminescent sensitivity response is much greater in the higher magnesium concentration dosimeters. This is probably due to the suppression of peak 2 and increase in the higher temperature peak 5 in which nearly all the thermoluminescent response occurs. In the lower dopant levels response is divided between two peaks whereas in the higher only one peak is dominant.

TABLE 5.1.

1st irradiation

Peak distance	Peak heights		Average
3.55	3.4 / 5.35	0.6355	
3.55	4.15 / 6.4	0.6484	
3.75	2.1 / 3.8	0.5526	
3.55	2.95 / 4.05	0.7283	
3.55	2.5 / 4.0	0.6250	0.6143
3.55	2.7 / 5.3	0.5094	
3.5	3.35 / 5.7	0.5877	
3.55	3.80 / 6.05	0.6280	

2nd irradiation

3.55	5.8 / 8.15	0.7116	
3.55	7.05 / 10.45	0.6746	
3.55	6.65 / 10.25	0.6487	
3.55	11.7 / 17.8	0.6573	
3.55	7.1 / 10.4	0.6826	0.6778
3.55	5.9 / 8.1	0.7283	
3.55	4.7 / 6.65	0.7067	
3.55	7.4 / 11.7	0.6324	
3.55	5.4 / 8.2	0.6585	

3rd irradiation

3.55	8.05 / 12.2	0.6598	
3.50	8.55 / 13.7	0.6240	
3.55	11.0 / 16.65	0.6606	
3.55	8.15 / 12.80	0.6367	
3.55	9.4 / 14.1	0.6666	0.6675
3.4	10.25 / 16.0	0.6406	
3.55	5.1 / 6.5	0.7847	

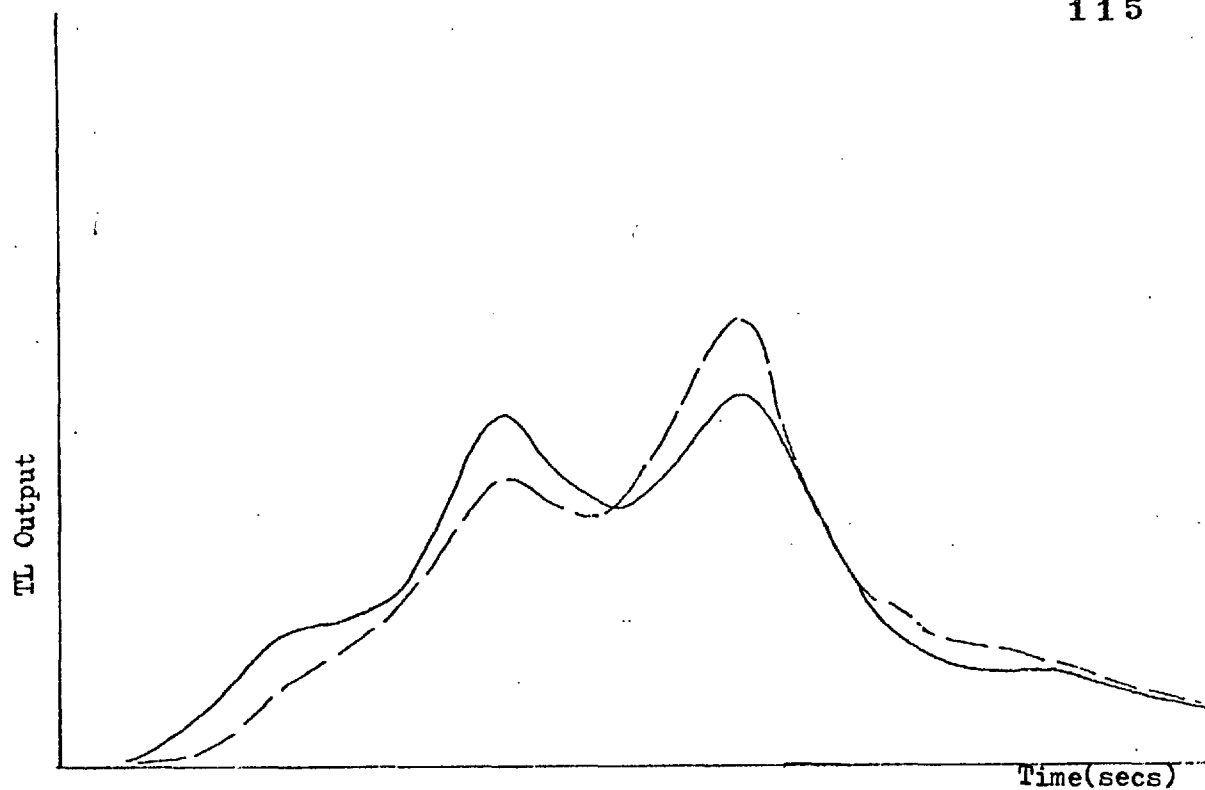
5.7. Effect of Re-irradiations on Heat Treated Dosimeters

The reference dosimeters exhibit the characteristic curves with two peaks corresponding to peaks 2 and 3. In both cases the low temperature peak is the smaller. The effect of quenching on the dosimeter is to alter the relative heights of the two peaks, the ratio of peak 2 to peak 3 being greater in the slow cooled specimens (Figure 5.9(i)). Repeated irradiations cause enhancement of the second peak in both cases (Figure 5.9(ii)) the overall shapes of curves however remain the same in that the slow cooled has the higher peak ratio.

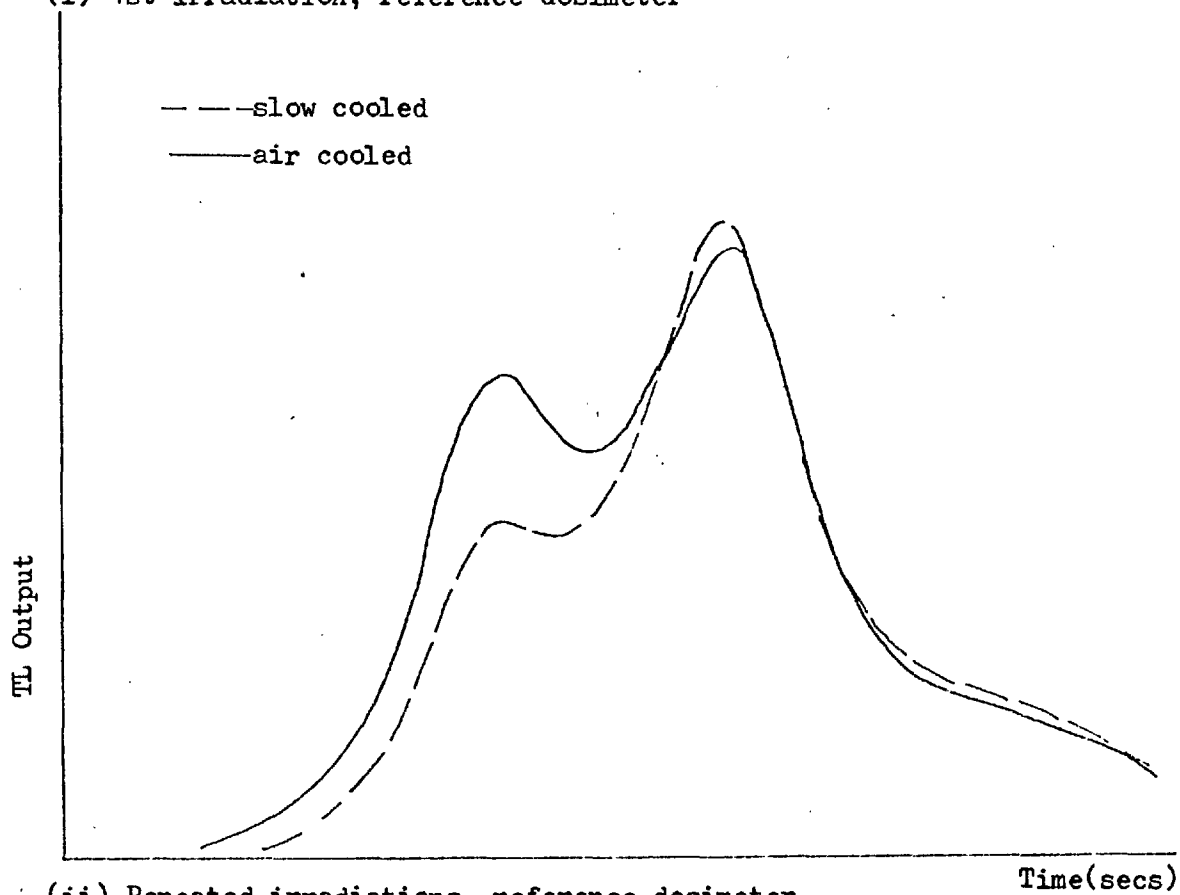
The 50 ppm (Figure 5.9(iii) and (iv)) dosimeters show very little difference in basic characteristic shape for the two treatments, the only major difference being in that of the thermoluminescent response- the quenched specimens would seem to be more sensitive.

As in the results obtained for heat treated single crystals in section 5.6 the 100 ppm specimens show the most marked difference in respect to slow cooling or air cooling, Figure 5.9(v). As in the single crystals the slow cooled samples show a second compound peak with a low temperature bias. The maximum corresponds to peak 4 and the bump to peak 3. The air cooled specimens show three defined peaks (compare with Figures 5.7(iii)). On re-irradiating the slow cooled specimen the compound peak is resolved and conforms to that of the air cooled specimens.

The 200 and 400 ppm specimens are unremarkable (Figures 5.9(vi) and (vii)) in that they exhibit the predictable glow curves. As in the 100 ppm specimens the response is greater in the air cooled specimens.

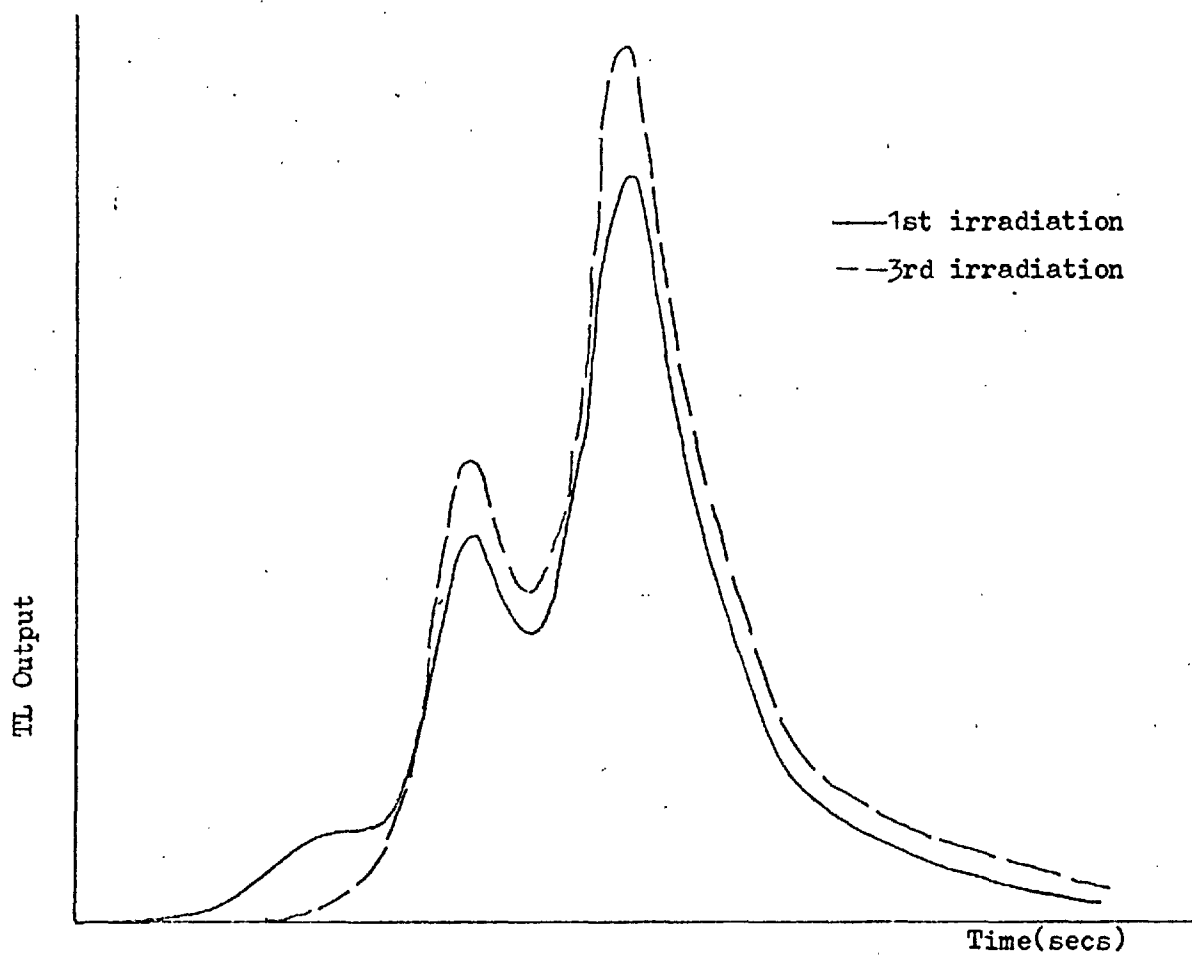


(i) 1st irradiation, reference dosimeter

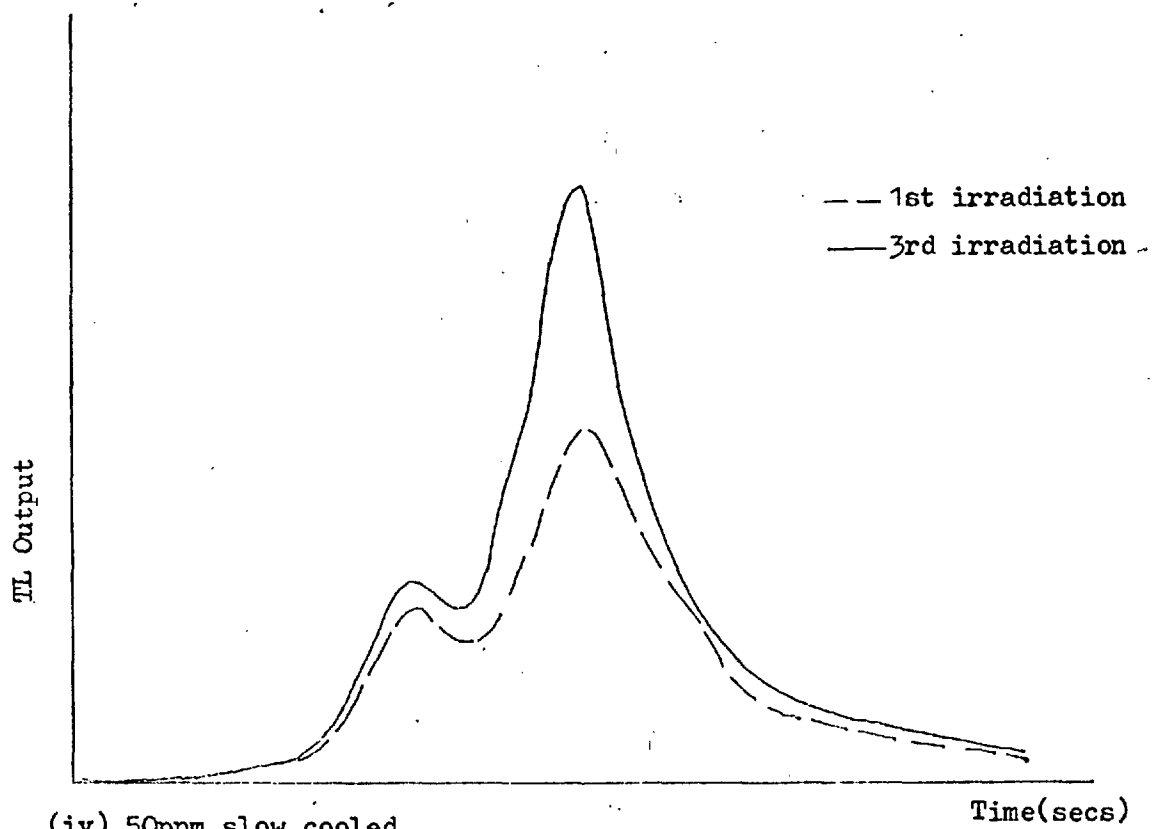


(ii) Repeated irradiations, reference dosimeter

Fig.5.9 Effect of Re-irradiations on Heat Treated Dosimeters.



(iii) 50ppm, air cooled



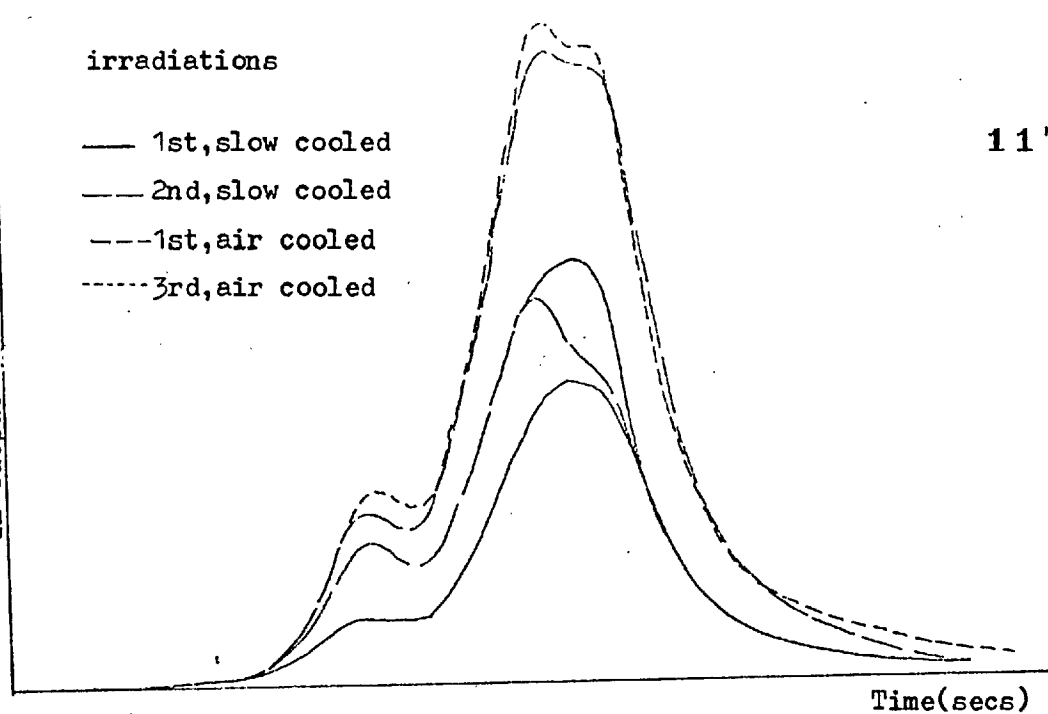
(iv) 50ppm, slow cooled

irradiations

— 1st,slow cooled
-- 2nd,slow cooled
---1st,air cooled
----3rd,air cooled

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TL Output

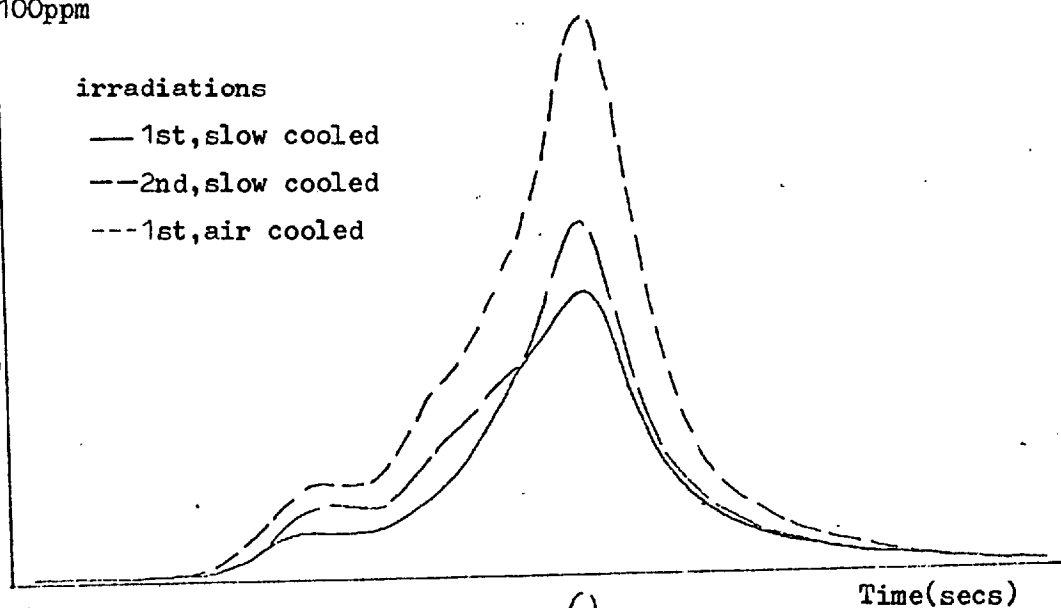


(v) 100ppm

irradiations

— 1st,slow cooled
-- 2nd,slow cooled
---1st,air cooled

TL Output

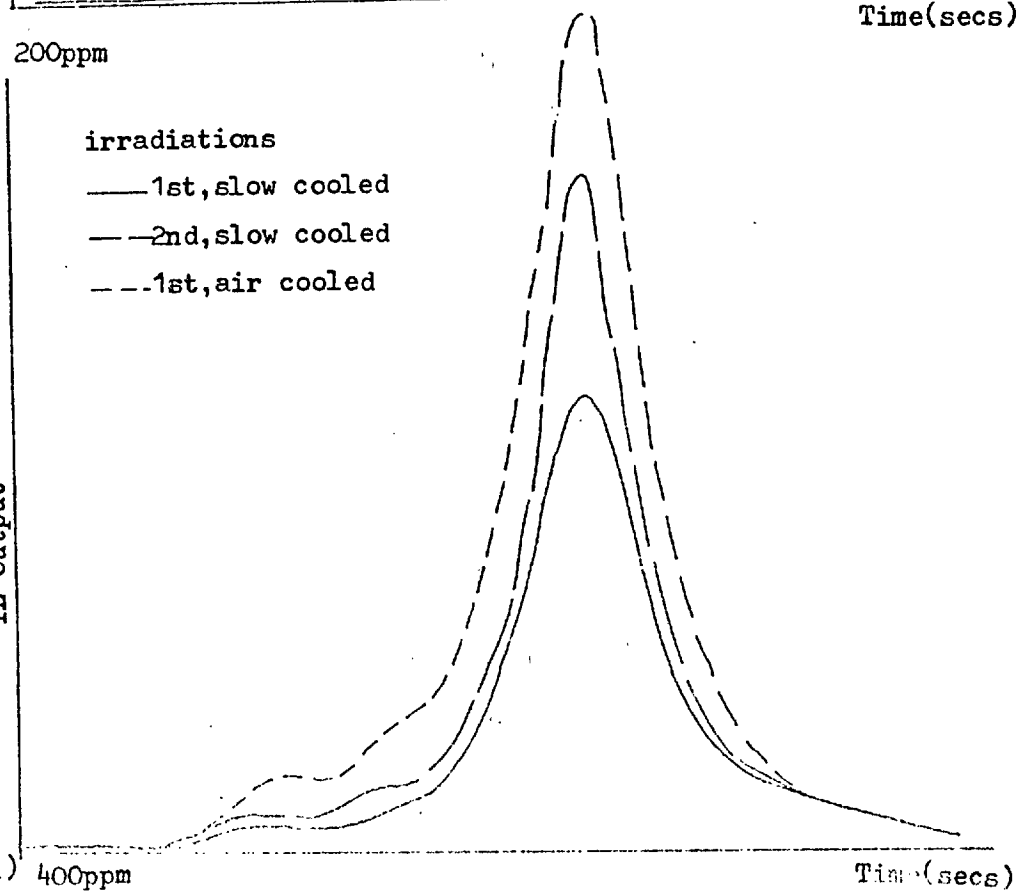


(vi) 200ppm

irradiations

— 1st,slow cooled
-- 2nd,slow cooled
---1st,air cooled

TL Output



(vii) 400ppm

Time(secs)

CHAPTER 6

General Conclusions

From the experimental research described in this work and from the results obtained some new facts can be shown to have emerged; others prove consistency with previous workers.

The most obvious conclusion concerns that of the magnesium concentration. As has been reported in all other investigations increasing the magnesium concentration causes a shift to the right in the resultant glow curve. The saturation point is around 400 ppm at peak 5. This has been interpreted in the past (73, 50, 51, 75) as showing that the lower peaks are probably caused by dipole cation-vacancy defects and that the higher peaks are due to higher order aggregates. Hence an increase in the amount of magnesium present will also increase the probability of higher order aggregate formation and peaks 4 and 5. The present work shows conclusive agreement with this. The glow curves produced by the lower concentration of magnesium have pronounced peaks 2 and 3 which one would expect if the cause was cation-vacancy dipoles, whilst the higher concentrations are mainly peaks 4 and 5. This also adds weight to the idea (31, 73) that peaks 2 and 3 and peaks 4 and 5 are really paired peaks each pair being caused by the same type of defect and not four separate defects causing four separate peaks. The form of the material does not affect the thermoluminescent response with regard to the magnesium concentration. The single crystals and the polycrystalline dosimeters both show the shift to the right with increasing magnesium concentration. Thus it can be inferred that the thermoluminescent response is primarily caused by chemical imperfections and not mechanically induced, although the latter can modify the resultant glow curves.

Future work could include dielectric loss measurements of the dosimeters along with optical absorption measurements. The former technique was initially started but had to be abandoned due to the time

available. It is not anticipated that results obtained from these techniques will produce any startlingly different conclusions since all previous research along these lines have also included at least one of the techniques described and used in the present research.

Repeated irradiations cause enhancement of thermoluminescent response. Attix (87) postulated a theory to explain this which has already been fully discussed in Chapter 2. The results shown here give good agreement with those anticipated. It is obvious that during the brief heating cycle during which the glow curve is produced not all the traps are emptied, hence increased sensitisation on re-irradiation. A saturation point, however, seems to be reached after the fifth such re-irradiation. More thorough investigation of the saturation level of sensitisation could be carried out - especially the apparent change in the dominant peak. (See Sections 5.6 and 5.7)

Dosimeters, as produced by the method described in this work, can and do enable radiation to be monitored in a more satisfactory way than single crystals. Early investigations (pre 1960) had to be abandoned because of the difficulty encountered in trying to obtain uniformly doped LiF; more recent work has also encountered the same problem. It is extremely doubtful whether a single crystal of LiF can be grown that has a uniformly doped cross-section. As has been shown the single crystals exhibit an apparent 'one peak' phenomenon and an apparent need to be shielded from daylight. The dosimeters do not.

Reproducible and consistent results can be obtained from the dosimeters. The best results, in that they are the most easy to interpret in terms of radiation received and hence useable by the layman, are produced by a standard anneal of 400°C for a minimum period of two hours followed by an air cool; easy procedures that can be carried out without sophisticated equipment and complicated involved training. More thorough investigation into the viability of using such dosimeters needs to be undertaken but

the results obtained in this work would seem to indicate that an economic dosimeter can be produced.

Suggestions for Future Work

1. Control of OH during growth of the crystals to study the effect on thermoluminescence. (see page 58)
2. Examination of the grain boundaries for porosity and the influence of the porosity on the microhardness and thermoluminescence. (see page 81)
3. Examination of the occurrence of the apparent 'one-peak' phenomenon. The results discussed here are in agreement with the initial work done by N.P.L. but not with the results obtained by the author in the paper attached. The current results are by far the more reliable.
4. Dielectric loss measurements on the current material (see Section 2.5)
5. Optical absorption measurements on the current material (see Section 2.6)
6. The saturation level of sensitisation *vis a vis* thermoluminescent response (see sections 5.6 and 5.7).

ACKNOWLEDGEMENTS

The author would like to express thanks to her supervisor, Professor P.L. Pratt for his encouragement, supervision and support throughout the investigation. She would also like to thank the National Physical Laboratory for making available the facilities for crystal growing and especially Dr. M. Rossiter and Dr. D. Rees-Evans for their help and advice during the initial stages of the research. The studentship granted by the Science Research Council and the facilities made available in the Department of Metallurgy and Materials Science by Professor J.G. Ball are gratefully acknowledged. Special thanks are expressed to Mr. H. Haddow for his technical assistance, my parents for their encouragement and to Mrs. G. Murray for her strenuous efforts in typing and finalising this thesis. Finally she would like to thank Dr. J. Nabarro without whose efforts this thesis would never have been finished.

Thermoluminescent Response of
Polycrystalline TLD-LiF Dosimeters

by

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Abstract

LiF single crystals have been grown with controlled Mg and Ti dopant levels. The thermoluminescent response of these crystals depended upon the composition; peaks 2 and 3 were dominant at low Mg concentrations, peaks 4 and 5 at high Mg concentrations. On crushing the single crystals into powder, the thermoluminescence was reduced, but after annealing at 400°C for 48 hours followed by air-cooling, this increased considerably. The powder was subsequently formed into translucent polycrystalline discs, of near-theoretical density, by a process of warm pressing, and the changes in thermoluminescent response were investigated. The nature of the thermoluminescence depends strongly upon the composition, as with the single crystals and the powders. In the pressed discs a new peak appears midway between peaks 3 and 4 for Mg concentrations of 100 and 200 p.p.m., and some characteristics of this peak are described. At higher Mg concentrations the principal peak both in powders and in pressed discs is peak 4; the effect of annealing at 400°C for 48 hours followed by air-cooling is to develop a prominent peak 5 at the expense of peak 4.

Introduction

Following the work of Rossiter, Rees-Evans and Ellis [1] at the National Physical Laboratory, Teddington, aimed at providing well-characterised thermoluminescent LiF powder, we have prepared polycrystalline dosimeters of near-theoretical density by a warm-pressing technique*. The aim of this paper is to compare the thermoluminescent response of LiF materials in the form of single crystals, powders, and polycrystalline discs, after a variety of heat treatments.

* Patent applied for.

Experimental Methods

Single crystals of LiF, doped with Mg and Ti, were grown by the Stockbarger technique in an argon atmosphere in the manner described by Rossiter, Rees-Evans and Ellis [1]. The starting material was vacuum-grown BDH LiF. The Mg concentrations were nominally 50, 100, 200 and 400 p.p.m. with 5 p.p.m. of Ti, and one crystal was grown with 400 p.p.m. of Ti and no Mg addition. Specimens for thermoluminescent study were prepared in the following forms:

- a. Cleaved discs of single crystals,
- b. Powders prepared from the single crystals by crushing,
- c. Powders warm-pressed to give translucent polycrystalline discs of near-theoretical density.

Specimens of the powders and the discs were annealed at 400°C for 48 hours and then either furnace-cooled, or air-cooled, to compare with untreated specimens.

The Imperial College ^{60}Co γ -source was used to give irradiations of 200 R. Glow curves were obtained using an Ecko Reader Head N.141B, with a TLD System C1600 made by Cirtronic Instruments (Reading) Ltd.; the linear heating rate was 1.4°C/sec. Specimens were reirradiated and read for a second and a third time without further heat-treatment to examine the effects of irradiation and read-out on the glow curves.

Experimental Results

(i) Single Crystals

These were irradiated in the as-grown condition with no further heat-treatment. The thermoluminescent response of the crystals varied with composition, and results for specimens containing 50, 100 and 400 p.p.m. Mg are shown in Figure 1. For 50 p.p.m. there is a marked peak 2, with a large peak 3 extending into 4; for 100 p.p.m., peaks 2 and 3 are small with a large peak 4, whereas with 400 p.p.m. peak 4 is small and peak 5 is the principal one. For 200 p.p.m. the response is mid-way between that for 100 and 400 p.p.m., showing largely peak 4.

(ii) Powdered Single Crystals

a. With no Further Heat-Treatment

The effect on the thermoluminescence of powdering sections of the single crystals is shown in Figure 2. As before, the response is strongly dependent upon the Mg addition, but the magnitude of the response is reduced by powdering, especially at high Mg concentrations. With 400 p.p.m., peak 5 is suppressed, and the response is confined to peak 4.

b. Annealed 48 Hours at 400°C, and Air-cooled

The effect of air-cooling from 400°C, shown by the dashed lines in Figure 2, is to restore the thermoluminescent response to a form similar to that of the single crystals, and to increase the intensity considerably. Specimens with 50 p.p.m. Mg have a distinct peak 2, with a large peak 3; with 100 p.p.m., there is a small peak 2, with a broad peak extending across both 3 and 4, whereas with 400 p.p.m. peak 5 becomes the principal one again.

c. Reirradiation of Air-cooled Powder

The second irradiation of specimens with 100 p.p.m. Mg reduced the thermoluminescent response but sharpened the broad peak extending across peaks 3 and 4, into three distinct peaks, shown by the dotted line in Figure 2. The outermost of the three are centred in peaks 3 and 4 respectively but the central peak is a new one, although it coincides with a distinct shoulder in the first irradiation of both untreated and air-cooled powders. This new peak 3₁ appears again in the pressed discs.

(iii) Powders Pressed into Discs

a. With No Further Heat-Treatment

The effect of pressing into discs, Figure 3, the powder with 50 p.p.m. Mg resembles that of air-cooling, but with an enhanced peak 2. With 100 and 200 p.p.m. Mg, peak 3₁ is prominent, together with lesser peaks 2, 3 and 4, while with 400 p.p.m. peak 4 predominates, as for the untreated powders. The effect of reirradiation, shown by the dashed lines in Figure 3, appears to be to destroy peak 3₁ in the discs with both 100 and 200 p.p.m. Mg.

b. Annealed 48 Hours at 400°C, and Air-cooled

The effect of air-cooling from 400°C, Figure 4, at low Mg concentrations is to enhance the thermoluminescent response, especially peak 3 in the 50 p.p.m. specimen and peak 3₁ in the 100 p.p.m. specimen. The most remarkable effect is seen in the 400 p.p.m. specimen, where, just as with the powders, air-cooling develops peak 5 almost entirely at the expense of peak 4. Peak 5 did not appear in pressed discs with 200 p.p.m. Mg even when air-cooled; the bulk of the response appeared in peak 4 as in the single crystals.

c. Reirradiation of Air-cooled Discs

On second irradiation, the air-cooled discs with 100 p.p.m. Mg behaved like the air-cooled powders, rather than the untreated discs. Peak 3₁ is enhanced, and in addition the level of peaks 2, 3 and 4 is increased. With 200 p.p.m. Mg the second irradiation of air-cooled discs produced little change, whereas with furnace-cooled discs a clear enhancement was found.

Discussion

We must emphasise that this is the first substantial set of results in our comparison of LiF in the form of single crystals, powders, and polycrystalline discs and many questions at this stage must go unanswered. Nevertheless, we feel that the present results show a number of features of interest and they should lead to a more definitive set of experiments in the future. The interesting features include the significant effect of Mg concentration, the suppression of peak 5 by heavy plastic deformation, and the appearance of the new peak 3 $\frac{1}{2}$.

(i) The Effect of Mg Concentration

While other workers must have studied the influence of Mg concentration upon the thermoluminescent response, the bulk of the published literature is concerned with TLD-100, with some 200 p.p.m. of Mg. Our initial experiments, following those at N.P.L., were carried out on a single crystal doped with 200 p.p.m. Mg and 5 p.p.m. Ti, and it appeared interesting to see what role the Mg has to play when added in larger and in smaller amounts. In all of the experiments, increasing the Mg concentration from 50 to 400 p.p.m. shifts the principal thermoluminescence from the low temperature peaks 2 and 3, towards the higher temperatures peaks 4 and 5. In these experiments it was not possible to observe peak 1 in view of the distance between the ^{60}Co γ -source and the reader unit. The other peaks were identified on the N.P.L. reader in specimens with 200 p.p.m. Mg and then identified on our own reader at a later date. The temperatures associated with the peaks using the Cirttronic Instruments System C1600 are given in the following Table.

Peak 2	98°C	Peaks 2 and 3 are commonly associated with the presence of free impurity-vacancy dipoles in the lattice and it is reasonable to expect a high proportion of these, compared with clusters of dipoles in the form of dimers or trimers, in specimens with but small Mg additions. With higher concentrations of Mg, the proportion of free dipoles present should be reduced, and those present as clusters, normally associated with peaks 4 and 5, should be greatly in the majority. Our experiments confirm these ideas and suggest that 400 p.p.m. is sufficient to maximise the response in peaks 4 and 5. More subtle effects of Mg concentration appear in the powders and in the pressed discs and these will be considered in the next section.
Peak 3	146°C	
Peak 3 $\frac{1}{2}$	168°C	
Peak 4	186°C	
Peak 5	212°C	

(ii) The Suppression of Peak 5 by Heavy Plastic Deformation

In our material the very heavy plastic deformation associated with crushing the single crystals into powders, and also with warm-pressing the untreated powders into polycrystalline discs, appears to eliminate the defects associated with peak 5 in specimens with 400 p.p.m. Mg. This suppression of peak 5 is in line with the effect of the gentler deformations of TLD-100 reported by Petralia and Gnani [2], and by Srinivasan and DeWerd [3], but crushing and pressing are more dramatic in their effect upon peak 5. The elimination of peak 5 by heavy deformation suggests that the peak involves well-arranged clusters of Mg impurity-

vacancy dipoles, which would be destroyed by the action of interpenetrating slip planes; whereas the continued existence of peak 4 implies a looser binding of the dipole clusters such as might occur by chance after crushing or pressing. If the dipoles retain their identity after deformation, and they are involved in peaks 2 and 3, then the suppression of 5 might well lead to an enhancement of peaks 2 and 3. However, this is not the case in our experiments save perhaps for the warm-pressed discs with 100 p.p.m. Mg. Annealing the deformed specimens at 400°C for 48 hours followed by air-cooling should restore a high concentration of dipoles, either free or clustered depending upon the Mg concentration. This treatment enhances peaks 2 and 3 at low Mg concentrations in keeping with the ideas outlined above. Even at such a low concentration as 50 p.p.m. Mg the effect of the air-cooling is to reduce the response in peak 4 shown by the untreated powders and discs, and also by the single crystals.

(iii) The Appearance of Peak 3½

An unexpected feature of our results is the appearance of peak 3½ in both the powders and the pressed discs containing 100 and 200 p.p.m. Mg. It is not noticeable in the single crystals of this composition so it must be associated with some defect configuration due to the heavy plastic deformation. There is no obvious reason for its appearance only in the 100 and 200 p.p.m. specimens and further work is necessary before its nature can be identified; for example can it be induced by smaller plastic deformations of the single crystals containing 100 and 200 p.p.m. Mg? From its position mid-way between peaks 3 and 4 it appears to be a species distinct from either free dipoles or clusters; one possibility might involve dipoles ordered in the long-range elastic-strain fields of dislocations, since the peaks occur only at high dislocation concentrations, and at low Mg concentrations where clustering is unlikely. The peak is enhanced by annealing at 400°C followed by air-cooling, especially in the pressed discs; this treatment would not reduce the dislocation density substantially, yet it would enable the concentration of free dipoles to return to a maximum after the heavy plastic deformation, and allow time for them to become oriented during the air-cooling. Furthermore, in the 100 p.p.m. discs, the effect of the heat-treatment is to enhance peak 3½ at the expense of peaks 2 and 3, in keeping with a reduction in the proportion of free, randomly-oriented, dipoles. It should be possible to check these ideas by further experiments and these may give some clue to understanding the obscure and conflicting effects of reirradiation.

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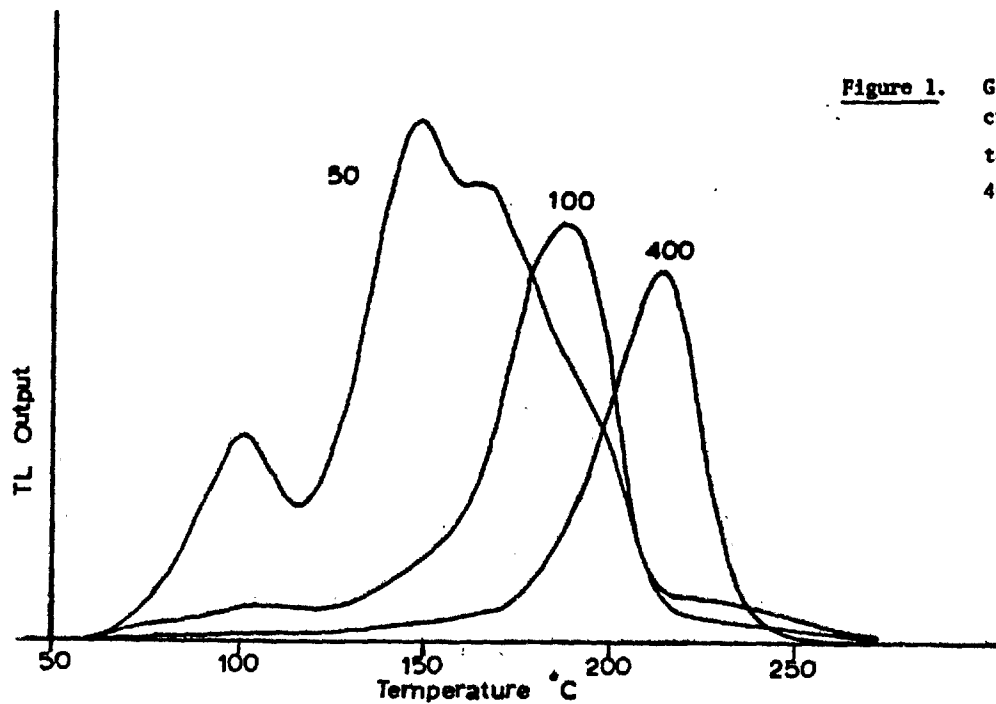


Figure 1. Glow curves of single crystals of LiF containing 50, 100, and 400 p.p.m. Mg.

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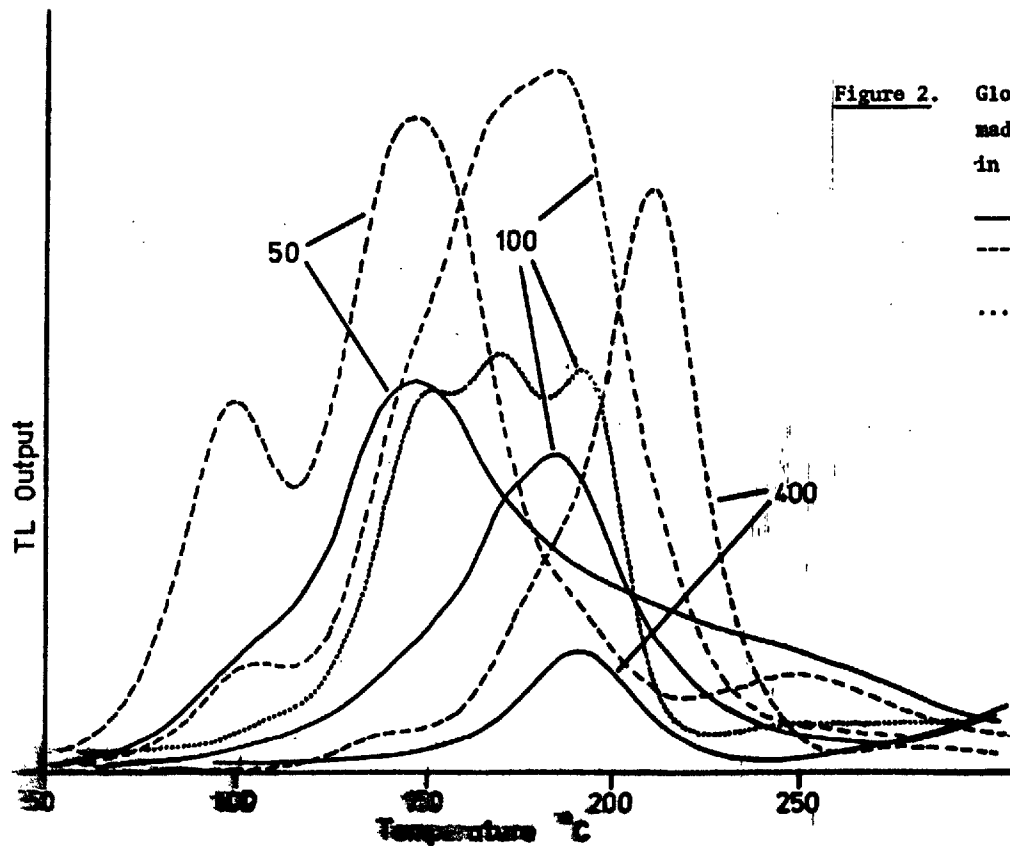


Figure 2. Glow curves of powders made from single crystals in Figure 1.

- Untreated
- - - - - Annealed 48 hours 400°C, air-cooled
- Annealed, air-cooled and reirradiated.

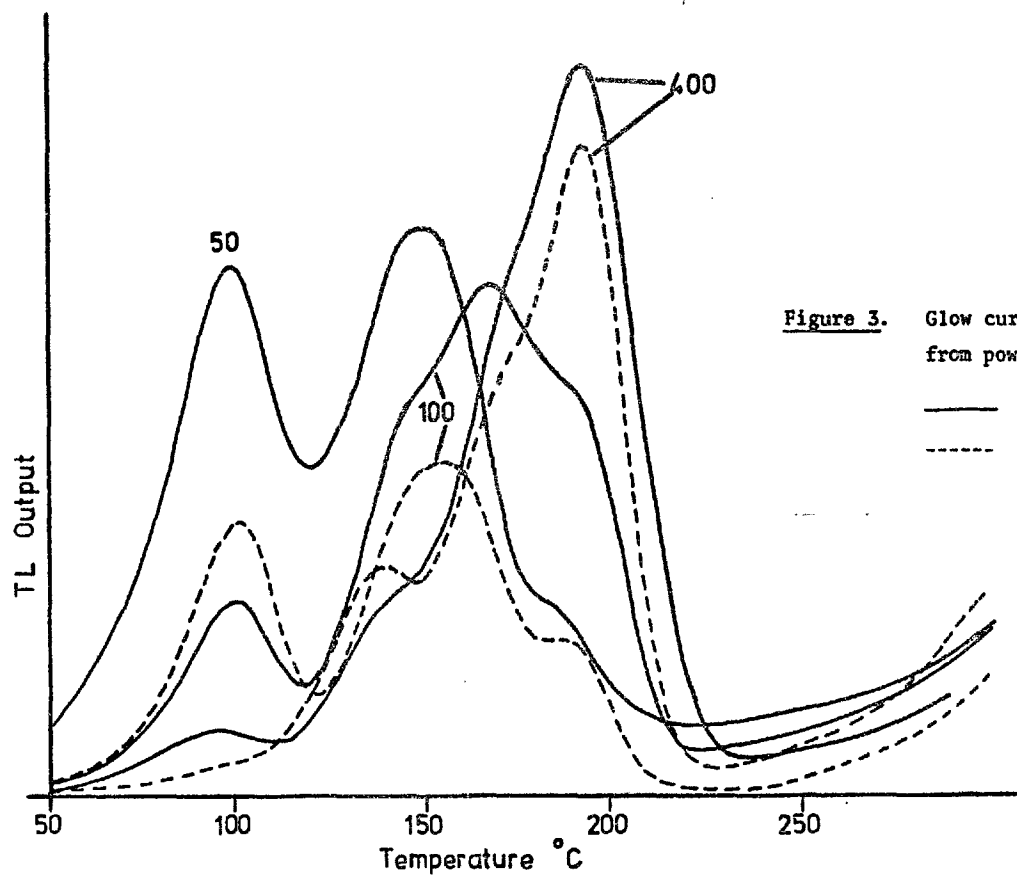
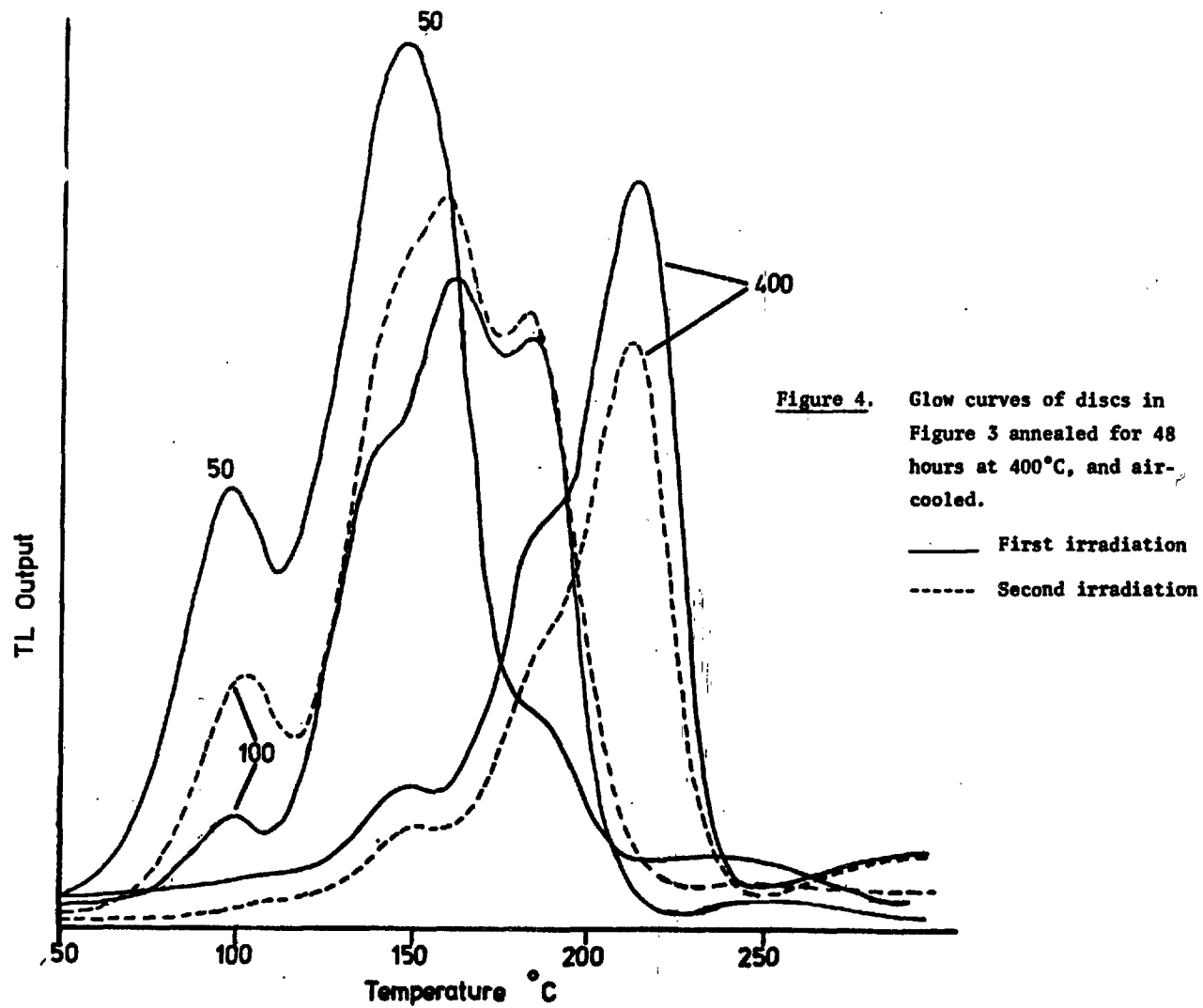


Figure 3. Glow curves of discs pressed from powders in Figure 2.

— First irradiation

- - - Second irradiation



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