

# Mechanism of thermoluminescence in magnesium oxide\*

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Thermoluminescence (TL) induced by  $\gamma$ -rays in nominally pure polycrystalline MgO powders has been investigated. In addition to a high temperature peak around 650 K, which is also present in the unirradiated specimens, TL glow peaks are observed around 365, 435, 510 and 545 K. The role of transition metal impurities on TL behaviour has been studied by the doping technique. It is observed that  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  act as emission centres while  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  act as quenchers. For a particular sample all  $\gamma$ -induced glow peaks give a similar emission spectrum which is characteristic of the activators present. Optical bleaching, isothermal decay and ESR studies have been used to study the trapping centres. It is shown that the charge carriers involved are holes from V-type defects. The dominant 365 K peak has been assigned to  $V_M$  centres. A hole-release mechanism involving recombinations with electrons trapped at activators is proposed to explain the TL behaviour.

## 1. Introduction

Thermoluminescence (TL) has been successfully used as an experimental tool for studying traps in crystals. Its applications in dosimetry, geology and archaeology have stressed the necessity for a basic understanding of the processes involved in this phenomenon. The main problems in such studies relate to the identification of trapping and emission centres, the nature of the charge carriers and the charge release mechanism. Despite considerable work [1-9] no consistent picture about TL of MgO has emerged as yet. Except for Cr and Fe impurities, which have been studied in some detail, the role of other transition metal and rare earth impurities has hardly been studied. Even in the case of Cr and Fe there exists a controversy particularly with respect to the blue ( $\sim 400$  nm) emission assigned both to  $\text{Fe}^{3+}$  and  $\text{Cr}^{2+}$  and the red ( $\sim 700$  nm) assigned variously to  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions. The identity of trapping centres is largely unknown for most glow peaks. In the present work, an attempt has been made to identify the role of impurities, and defect centres in the TL

of MgO using glow curves, emission spectra, ESR, optical bleaching and isothermal decay studies.

## 2. Experimental

The polycrystalline MgO powders used in this work were prepared by thermal decomposition of  $\text{Mg}(\text{OH})_2$  precipitated from reagent grade  $\text{MgSO}_4$  solution using concentrated  $\text{NH}_4\text{OH}$ . Samples doped with  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  were prepared by the co-precipitation technique. A semi-quantitative spectroscopic analysis showed the following impurities (in p.p.m.): Cr ( $< 5$ ), Mn ( $< 5$ ), Fe ( $< 25$ ), Ni (5), Cu (50), Pb (10), Zn (100) and Al ( $< 50$ ). The glow curves were recorded in the 300 to 750 K region using the apparatus described elsewhere [10]. The heating rate used was  $3 \text{ K sec}^{-1}$ . The emission spectra were recorded at a scanning rate of  $100 \text{ nm min}^{-1}$  by incorporating a Jarrel Ash grating monochromator coupled to an EMI 9558QB photomultiplier tube which served as the detector. For optical bleaching studies, a 100 W Bausch and Lomb tungsten lamp (model 33-86-44) along with a 1 cm thick water filter and an Ealing OB2 colour filter was used.

\*Based on the thesis submitted by A. Sathyamoorthy to the University of Bombay (1976).

The distance of the sample from the light source was about 30 cm.  $\gamma$ -irradiation was done using a  $^{60}\text{Co}$   $\gamma$ -source with a dose rate of  $0.3 \text{ Mr h}^{-1}$ . ESR spectra were recorded on a Varian V-4502 X-band spectrometer having a dual sample cavity. About 30 mg of powder was used in a  $15 \text{ cm} \times 0.2 \text{ cm}$  thin pyrex tube.

### 3. Results

#### 3.1. Glow curves and emission spectra

Fig. 1 gives the typical glow curve of the undoped MgO after 1 h of  $\gamma$ -irradiation, with overlapping glow peaks around 365, 435, 510, 545 and 650 K. The high temperature glow peak around 650 K, invariably present in all unirradiated MgO samples, has been studied previously in detail by the authors and has been attributed to adsorption [11, 12]. Hence only the other  $\gamma$ -induced TL peaks are discussed here.

The general pattern of the glow curve was similar in all the doped samples. Also, no new peak attributable exclusively to any of the dopants was present. In the case of  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  (0.001 mol%) doped specimens all these peaks were enhanced in intensity. Concentration quenching, however, was found to set in at concentrations above 0.01 mol%. For the lowest dopant concentration (0.001%) in  $\text{MgO}:\text{Ni}^{2+}$  no significant enhancement was seen. In the case of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$

and  $\text{Cu}^{2+}$  dopants considerable quenching of TL intensity was observed and TL was not detected above 0.05% dopant concentration.

In order to determine the role of impurities, the TL emission spectra of various peaks were recorded. Figs. 2 and 3 show the emission spectra of the 365 K peak in different doped and undoped samples. Two main broad emission bands are in general seen in the undoped samples.  $\text{Cr}^{3+}$  preferentially enhances the 700 nm band and shows some vibrational structures (Fig. 2, Curve 3).  $\text{Mn}^{2+}$  similarly gives a strong orange emission near 600 nm and  $\text{Ni}^{2+}$  a blue-green emission near 490 nm. From fluorescence studies these are known to be the characteristic emission of the respective dopants in MgO. In contrast, no new emission bands are seen in the case of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  but only a reduction in intensity of the original bands from the undoped samples.

#### 3.2. Optical bleaching

In certain cases, it is possible to supply activation energy to TL peaks by optical means. However, difficulties arise when different traps have overlapping absorption bands. In MgO the role of F- and V-type defects can be distinguished by optical bleaching, as these have widely separated absorption bands ( $\sim 250$  and  $540 \text{ nm}$  respectively). Ionizing radiations can populate predominantly only

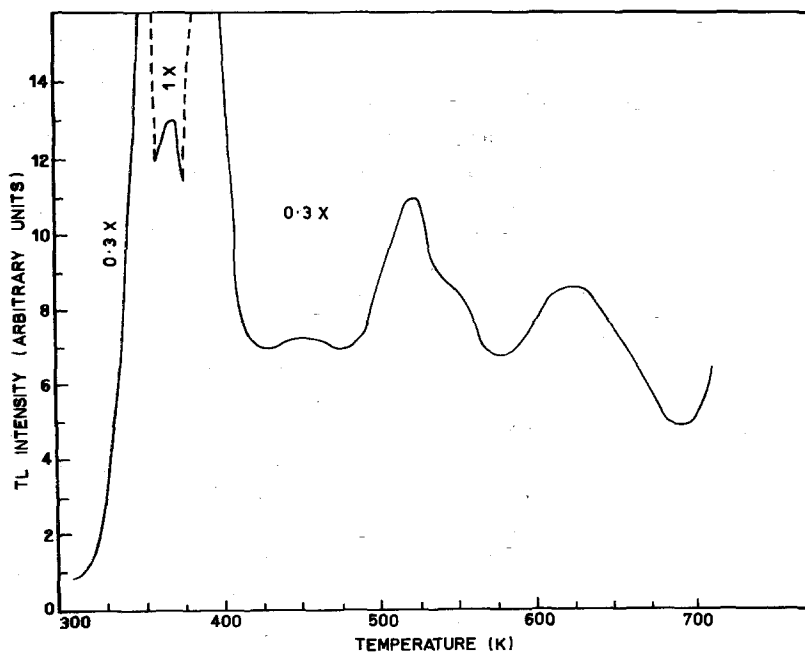


Figure 1 Glow curve of  $\gamma$ -irradiated MgO.

Figure 2 TL emission spectra of 365 K peak recorded at 338 K. Curve 1, undoped MgO. Curve 2,  $Mn^{2+}$  (0.01%) doped MgO. Curve 3,  $Cr^{3+}$  (0.01%) doped MgO.

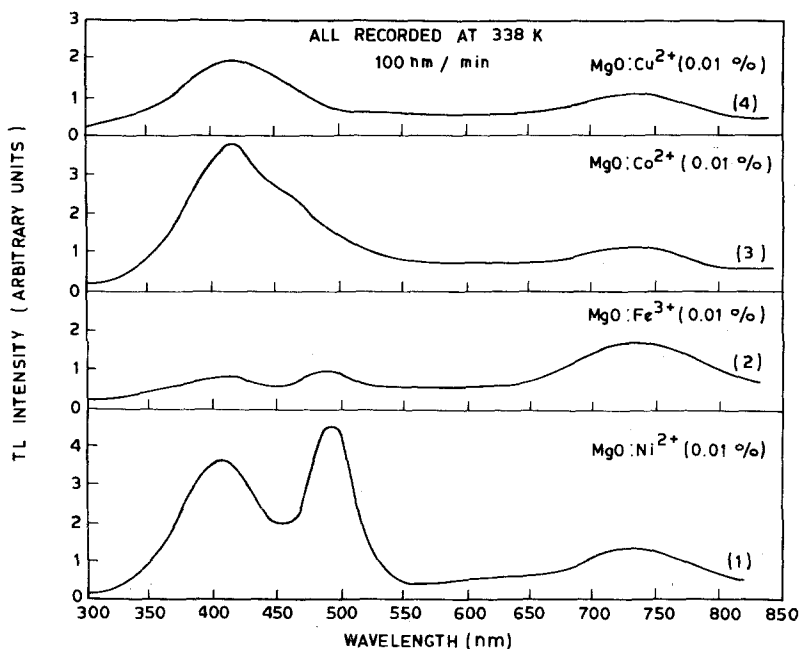
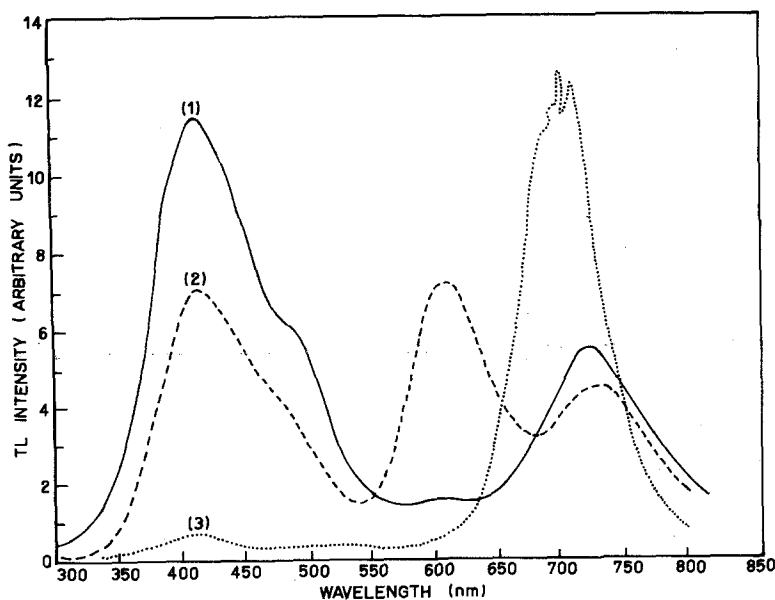


Figure 3 TL emission spectra of 365 K peak recorded at 338 K in various impurity-doped MgO samples.

the cation vacancy centres in their different charge states and environments in MgO, and hence their role in TL was studied.

Samples were bleached with green light using Ealing OB2 filter whose transmission spectrum ( $\lambda_{max} = 500$  nm) matched fairly well with the known absorption spectra of the V-defects such as  $V_{OH}$ ,  $V^-$ ,  $V$ ,  $V_M$  (notation after Sonder and Sibley [13]) in MgO. Glow curves of thin powder layers of irradiated MgO were compared before and after bleaching. Fig. 4 shows the result as percentage of

peak height bleached versus duration of illumination for bleaching. Intensity of all  $\gamma$ -induced peaks were found to be reduced by bleaching. It is noted that initially ( $< 20$  min) the 510 and 545 K peaks bleach faster than the 365 K peak and in 2 h 80 to 90% of each of the peaks is bleached out.

More information on the nature of charge carriers of the different peaks was obtained by the optical re-excitation technique. The major 365 K peak was thermally annealed out at 375 K

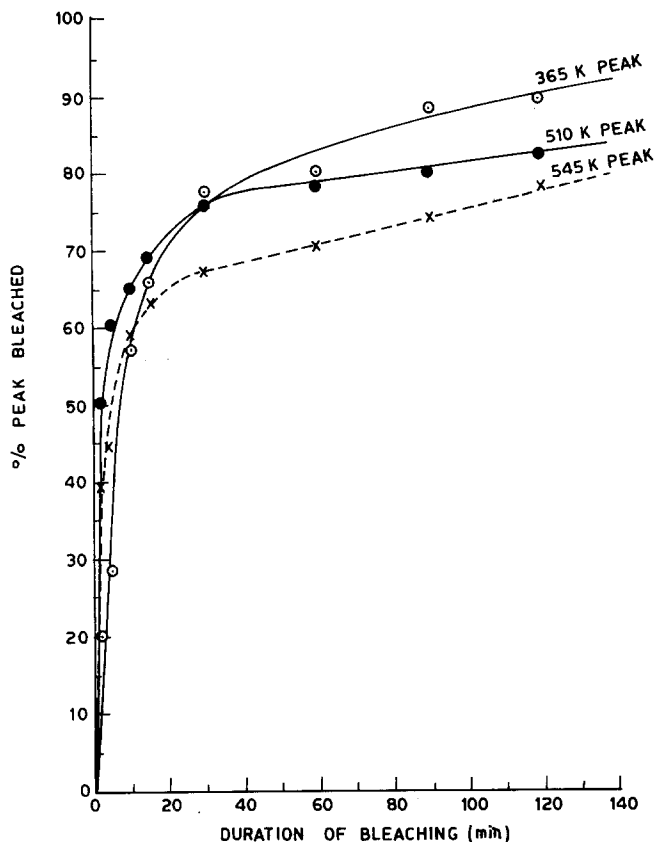


Figure 4 Bleaching behaviour of TL glow peaks of MgO.

and this partially annealed sample was then bleached with green light at room temperature for 10 min, and its glow curve was recorded. The 365 K peak reappeared (although with reduced intensity) and the higher temperature peaks suffered a corresponding reduction in intensities. This suggests that charges from the populated traps were partially transferred to the empty traps, thereby indicating that the same type of charges are involved in this transfer.

### 3.3. Isothermal decay studies

Isothermal decay offers a very useful means of studying the kinetic behaviour of TL peaks since this is the only method not affected by the variation in luminescence quantum efficiency with temperature. The decay kinetics of the 365 K peak has been a subject of great controversy. Both first- and second-order behaviour have been attributed to this peak with a wide range of trap depths and frequency factors. Most results were based on application of the first order decay law without consideration of the experimental validity of the model used. In this work general kinetic order

equation proposed by May and Partridge [14] has been used to fit the decay data.

Fig. 5 shows the plot of  $\log(\text{TL})$  versus time of decay at 298 K of the 365 K peak. It was observed that neither the first- nor the second-order equations nor any fractional order could fit the observed data satisfactorily. The initial few hours of decay showed very significant deviations from a straight line. Following the first order superposition theory the decay data could be fitted only by two exponential components with half lives of 2.2 h and 15.3 h as seen in Fig. 5. Such a behaviour is characteristic of the decay of  $V_M$  centres which have been reported [16] from independent ESR and optical absorption data to have two first-order decay components with half lives of 10.5 and 15.4 h. Wertz [15], Kapper *et al.* [16] and Tench *et al.* [17] have reported a half-life of 2 to 15 h for  $V_M$  centres.

### 3.4. ESR studies

One of the most efficient activators and an invariably present impurity in alkaline earth oxides, is the  $\text{Cr}^{3+}$  ion. TL emission spectra had clearly

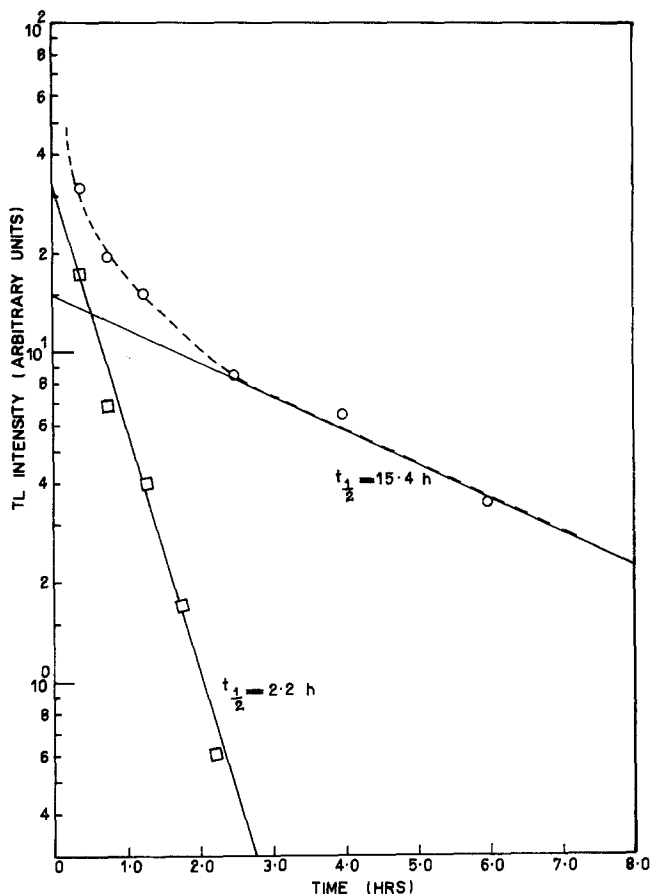


Figure 5 Decay curve of 365 K peak at room temperature. The solid lines show the two exponential components of the curve.

identified this ion as the emission centre for TL peaks. ESR studies were therefore carried out to correlate with TL.

ESR spectra were recorded before and after  $\gamma$ -irradiation as well as after annealing out TL peaks successively at 350, 420, 535 and 635 K. The height of the  $\text{Cr}^{3+}$  cubic line at  $g = 1.9800$  was taken as a measure of the  $\text{Cr}^{3+}$  concentration and compared with TL intensity. Fig. 6 shows the ESR spectra before and soon after irradiation. The relative heights of the signals are given as numbers in parentheses in the figure. It is seen that  $\sim 70\%$  reduction in  $\text{Cr}^{3+}$  concentration is obtained after 18 h of  $\gamma$ -irradiation. Fig. 7 shows the ESR spectra after room temperature decay for 24 h and after successive annealings at 350, 420, 535 and 635 K when the corresponding TL peaks were annealed out. There is an increase in  $\text{Cr}^{3+}$  concentration after each annealing of the glow peak. It is also to be noted that even after the last peak has been annealed out, the ESR signal intensity has not recovered to the original level of the unirradiated sample.

## 4. Discussion

### 4.1. The role of impurities

The fact that for the different doped samples the glow curve pattern was the same with respect to the number of TL peaks and their position shows that the trapping centres of these peaks are a property of the host lattice. This behaviour is similar to that observed in rare earth doped  $\text{CaF}_2$  by Merz and Peshan [18], where the traps were

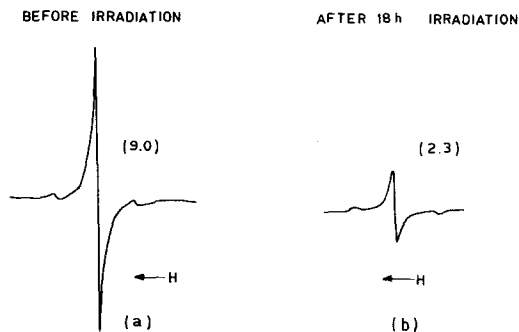


Figure 6 Effect of  $\gamma$ -irradiation on the ESR spectrum of  $\text{MgO}:\text{Cr}^{3+}$  (0.01%).

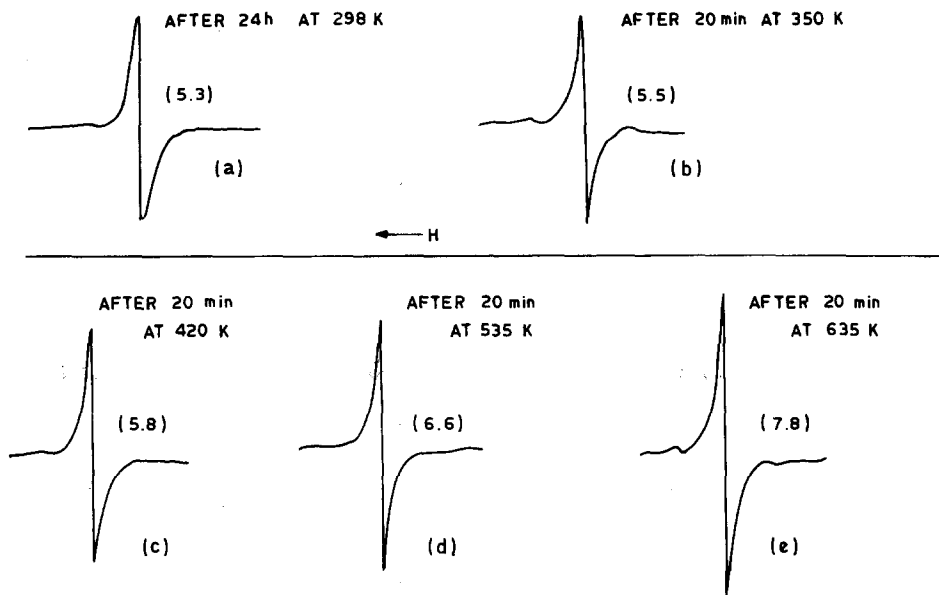


Figure 7 ESR spectra of  $\text{MgO}:\text{Cr}^{3+}$  (0.01%) after TL annealings at different temperatures.

identified with defect centres in the host lattice.  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  enhanced TL intensity and gave their characteristic emissions and hence are identified as emission centres.  $\text{Ni}^{2+}$  also is probably an emission centre for TL peaks, although no enhancement was seen in TL glow curve, which in turn could be due to the concentration quenching effect. Neither new TL peaks nor new emission bands were detected in the case of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  dopants. Instead only suppression of the original peaks/emission bands was observed in these cases and hence they are identified as quenchers. In other luminescence studies [19, 20] visible emission bands have not been reported for  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  in MgO.

The role of  $\text{Fe}^{3+}$  is however a subject of controversy. It has been considered an emission centre as well as a quencher. A blue emission ( $\sim 400$  nm) and a red emission ( $\sim 700$  nm) have been reported by many workers [1–6] in TL of MgO. The origin of the blue emission is not yet clearly established despite some assignments to  $\text{Fe}^{3+}$  and  $\text{Cr}^{2+}$ , while the red one has now been fairly well established to be due to  $\text{Cr}^{3+}$  and not  $\text{Fe}^{3+}$ . In our specimens,  $\text{Fe}^{3+}$  doping suppressed both these emission bands and also the total TL peak intensity. Even in single crystals ( $< 5$  p.p.m. iron) where iron is normally present as the  $\text{Fe}^{2+}$  ion, experiments to increase the  $\text{Fe}^{3+}$  concentration by drastic oxidation in air at 1575 K for 40 h resulted in total suppression of all TL, indicating that  $\text{Fe}^{3+}$  does not act as an

activator or emission centre for TL. It may be pointed out that Ziniker *et al.* [21] failed to observe any blue TL emission (assigned to  $\text{Fe}^{3+}$  by some workers) in relatively pure as well as iron doped MgO.  $\text{Fe}^{3+}$  has been considered a quencher of luminescence in many other lattices also [22–26].

#### 4.2. The defect centres and TL

In MgO the most important defect is the positive ion vacancy which forms V-type defects capable of existing in different charge states and environments. At room temperature a majority of these are associated with nearby trivalent cation impurities such as  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ . On irradiation these trap one or more holes to form defect centres more important of which are  $V_M$ ,  $V^-$ ,  $V$  since these are thermally stable above room temperature. In  $\gamma$ -irradiated MgO the predominant defects are of the V-type as hardly any F-type centres are produced by  $\gamma$ -irradiation in MgO.

These centres absorb light in the 370 to 825 nm region with almost completely overlapping bands peaking around 535 nm. The work reported in Section 3.2 showed that all TL peaks could be bleached out with this light, thus indicating that the TL peaks were associated with V-centres. This was further supported by the optical re-excitation studies indicating that the same type of charges (i.e. holes) were involved in the TL peaks.

As for the main 365 K peak, the traps are identified with  $V_M$  centres. This is supported by

the following: (i) Although earlier workers have assigned  $V^-$  centre to this peak this is considered an unlikely candidate since it is now established [15, 16] that the pure  $V^-$  centres are remarkably stable in the dark at room temperature and only a small decrease is observed in their concentration over a period of two years. On the contrary the TL peak decays within a few hours.

(ii) Independent ESR studies [16] have shown that the concentration of pure  $V^-$  centres increase at the cost of  $V_M$  centres when the irradiated sample is heated at 323 K. The TL peak rapidly decays at this temperature and hence  $V^-$  centres cannot be trapping centres for this peak and

(iii) The decay behaviour of  $V_M$  centres has a striking similarity with the decay behaviour of the TL peak, as detailed in Section 3.3. It may also be mentioned in passing that it has been observed earlier [27] that reactor irradiation suppresses this TL peak, again in agreement with the fact [15] that in neutron irradiated MgO there is a lack of impurity associated  $V^-$  centres (i.e.  $V_M$  centres) and a preponderance of isolated and other complex V-defects.

### 4.3. The mechanism

From the foregoing observations it emerges that the emission centres for all the observed TL peaks in MgO powder are the inherent traces of  $Cr^{3+}$ ,  $Mn^{2+}$  and  $Ni^{2+}$  impurities. The trapping centres which are not affected by ambients are the variety of V-type defects produced in the host lattice by irradiation, of which the  $V_M$  centres are assigned to the 365 K peak. It is therefore reasonable to visualize a hole-release mechanism for TL: holes from V-type defects recombine with electrons trapped at activator ions, the recombination energy exciting the latter to the excited states. The subsequent relaxation of the activator ions to the ground state causes the TL emission observed. More direct evidence for recombination taking place at activator sites has been given in Section 3.4 by the ESR data for MgO:  $Cr^{3+}$ .

The reduction in  $Cr^{3+}$  concentration on irradiation and its gradual increase on TL heating indicates direct participation of  $Cr^{3+}$  in the charge transfers involved in TL. The incomplete recovery of  $Cr^{3+}$  concentration in the temperature range of TL emission is believed to be associated with some  $Cr^{2+}$  formation which causes the blue 400 nm emission [4, 28, 29]. A similar incomplete

recovery was noticed by Sibley *et al.* [5] but they did not attempt to explain the same.

The changes in the  $Cr^{3+}$  concentration can be visualized in terms of conversion of  $Cr^{3+}$  into a different valence state and its recovery on TL heating. Available data [4, 6, 29] show this valence state to be  $Cr^{2+}$  formed after irradiation. Thus  $Cr^{3+}$  is considered to act as an electron trap; and V-type defects as hole traps for TL. While for the major 365 K peak the hole is due to the  $V_M$  centres, other hole traps are involved for the higher temperature peaks. Since  $Mn^{2+}$  and  $Ni^{2+}$  also show a similar TL behaviour, the same mechanism is considered to be operative in these cases too.

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