CHAPTER IV

THERMOLUMINESCENCE
Many phosphors, when heated after suitable excitation at a temperature, show a complex variation of intensity as the temperature rises; this phenomenon is known as ‘thermoluminescence’ (TL).\(^{(1)}\) It differs from phosphorescence in the sense, that the latter occurs at a fixed temperature whereas in the case of TL, the temperature changes. In fact thermal energy is responsible for the liberation of trapped electrons and holes in both the cases.

In the TL process, the phosphor is excited at a sufficiently low temperature until all the traps are filled. The phosphor is then allowed to decay for a sufficient time so that the shallower traps are emptied and only the deeper traps remain filled. After heating the phosphor at a constant rate now, the traps filled during excitation are emptied, releasing the frozen-in luminescence. The plot of luminescence intensity versus temperature is known as ‘glow curve’ which shows a peak for each group of traps. Thus TL can in principle be used to gain better understanding about the exact nature of trapping states such as trap depths and their distribution etc.\(^{(2-4)}\) Shionoya et al.\(^{(5)}\) have attempted to estimate the number of filled traps from the glow curve area.

4.2 Theories of TL

The first theoretical treatment for a well isolated TL
peak was given by Randall and Wilkins\(^{(5)}\) on the basis of a monomolecular mechanism and assuming a uniform heating rate and absence of retrapping. The equation given by them was:

\[
I = -C \left( \frac{dn}{dt} \right) = C n S \exp \left( -\frac{E}{kT} \right) \tag{4.1}
\]

where \(I\) is the TL intensity, \(S\) is a constant (having the dimension of \(\text{sec}^{-1}\)) called the 'escape frequency factor', \(n\) is the concentration of trapped electrons, \(T\) is the absolute temperature, \(k\) is Boltzmann's constant and \(C\) is a proportionality factor which can be set equal to unity without any loss of generality. The solution of the differential equation (4.1) is

\[
n = n_o \exp \left[ -(S/\beta) \int_{T_0}^{T} \exp \left( -\frac{E}{kT} \right) dt \right] \tag{4.2}
\]

where \(n_o\) is the initial concentration of filled traps and \(\beta\) is the heating rate \(\frac{dT}{dt}\). Assuming \(C = 1\) this gives for the TL intensity

\[
I = n_o S \exp \left( -\frac{E}{kT} \right) x \exp \left[ \left( \frac{-S}{\beta} \right) \int_{T_0}^{T} \exp\left( -\frac{E}{kT} \right) dt \right] \tag{4.3}
\]

By differentiating and equating to zero, one finds the condition for the maximum:

\[
\beta \frac{E}{k} T_m^2 = S \exp \left( -\frac{E}{kT_m} \right) \tag{4.4}
\]

where \(T_m\) is the temperature at the glow peak maximum. Knowing \(S\), this could serve as a transcendental equation to be solved.
numerically for $E$.

Another approximation, more suitable for some of the glow peaks was given by Garlick and Gibson$^{(7)}$ and is represented by the equation:

$$I = -\frac{dn}{dt} = S' n^2 \exp (-E/kT) \quad (4.5)$$

where $S'$ is a constant with dimension of $\text{cm}^3\text{sec}^{-1}$. This case is usually referred to as 'second order kinetics'. According to Garlick and Gibson, the second order approximation applied when retrapping and recombination probabilities are equal. The solution of (4.5) is:

$$I = n_0^2 S' \exp (-E/kT) \times \left[ 1 + (n_0 S'/\beta) \int_{T_0}^{T} \exp(-E/kT)dt \right]^{-2} \quad (4.6)$$

The term in brackets in (4.6) as well as the right hand exponential term in (4.3), varies only slightly at temperatures low in comparison to $T_m$. Therefore $I$ is proportional, in this region, to $\exp(-E/kT)$. This provides a simple means for calculating the activation energy from the slope derived from a plot of $\log(I)$ versus $1/T$ in the 'initial rise' region.$^{(7,8)}$ The initial rise method is expected to be valid for intermediate order kinetics as well.$^{(9)}$ However, some theoretical$^{(10,11)}$ as well as experimental reasons limit its use.

4.3 Evaluation of trap depth $E$

Of the various methods developed for calculating the
trap depth, a few are given below.

The first method for calculating activation energies by TL curves was given by Jrbach\(^{(13)}\), who found empirically that a reasonable estimate for the trap depth \( E \), in electron volts is given by:

\[
E = \frac{T_m}{500}
\]

(4.7)

where \( T_m \) is the temperature of the glow curve maximum in absolute units.

Randall and Wilkins\(^{(5)}\) used the relation (4.4) which can be put in the form:

\[
E = k T_m \left[ 1 + f(S, \beta) \right] \log S
\]

(4.8)

where

\[
f(S, \beta) = \log \left( \frac{k T_m^2}{\beta E} \right) / \log S
\]

(4.9)

is a small correction factor of the order of 0.1 and may be neglected. Thus

\[
E = 2.303 k T_m \log_{10} S
\]

(4.10)

Curie\(^{(14)}\) has proposed a formula which holds good at relatively lower heating rates:

\[
E = \frac{T_m (0K) - T_\beta(S)}{\Theta(\beta/S)}
\]

(4.11)

where \( T_0 \) and \( \Theta \) are constants dependent on the parameter \( \beta/S \). The values of these constants for a particular value of \( \beta/S \) can
be obtained graphically with the help of a Table 4.1 provided by him. In this method trap depth evaluation depends upon the accuracy of S.

Booth, Bohun and Parfianovitch\(^{15-17}\) have shown independently that by using two heating rates \(\beta_1\) and \(\beta_2\), S can be eliminated. If the glow peaks corresponding to \(\beta_1\) and \(\beta_2\) are \(T_{m1}\) and \(T_{m2}\) respectively, then the trap depth is given by:

\[
E = \frac{k \log \beta_1/\beta_2 (T_{m2}/T_{m1})^2}{1/T_{m2} - 1/T_{m1}}
\]  \(4.12\)

where \(\beta_1 > \beta_2\) and \(T_{m1} > T_{m2}\)

\[
\log kS/E = \frac{T_{m2} \log(T_{m2}/\beta_2) - T_{m1} \log(T_{m1}/\beta_1)}{T_{m1} - T_{m2}}
\]  \(4.13\)

Since the peak temperature varies only slightly with heating rate, the method is not very precise.

A number of methods for calculating trap depths are based on measurement of \(T_m\), the temperature at the maximum, and \(T_1\) and \(T_2\) the first and second half-intensity temperatures. The formulae for finding \(E\) by these methods usually contain one of the following factors: (a) \(\gamma = T_m - T_1\) the half width on the low temperature side of the peak, (b) \(\delta = T_2 - T_m\), the half width towards fall off of the glow peak, or (c) \(\omega = T_2 - T_1\),
the total half width. By assuming that the area of the half peak toward the fall off is equal to the area of a triangle having the same height and half width, Lushchik\textsuperscript{(18)} showed that the trap depth can be given by:

\[ E = k \frac{T_m^2}{\delta} \]  \hspace{1cm} (4.14)

Once \( E \) is calculated by any method, insertion into equation (4.4) gives the value of escape-frequency factor:

\[ S = \left( \frac{\beta}{\delta} \right) \exp \left( \frac{T_m}{\delta} \right) \]  \hspace{1cm} (4.15)

For second order kinetics, Lushchik found by the same assumption:

\[ E = 2k \frac{T_m^2}{\delta} \]  \hspace{1cm} (4.16)

Halperin and Briner\textsuperscript{(9)} found two general equations for evaluating the trap depth, one for carriers raised into a level within the forbidden gap,

\[ E = \left( \frac{q}{\delta} \right) k \frac{T_m^2}{\delta} \]  \hspace{1cm} (4.17)

and another for excitation into the band

\[ E = \left( \frac{q}{\delta} \right) k \frac{T_m^2}{\delta} \left( 1 - \Delta \right) \]  \hspace{1cm} (4.18)

where \( \Delta = \frac{2kT_m}{E} \) is a correction factor usually of the order of magnitude of 0.1. The value of \( q \) depends upon the order of process. For first order kinetics

\[ q_1 = 1.72 \mu \gamma \left( 1 - 1.58 \Delta \right) / \left( 1 - \mu \gamma \right) \]  \hspace{1cm} (4.19)
and for second order

\[ q_2 = 2 \mu g \left( 1 - 2\Delta \right) / \left( 1 - \mu g \right) \]  \hspace{1cm} (4.20)

where \( \mu g = \frac{\delta}{\omega} \) was used by Halperin et al.\(^{(19)} \) for evaluating the order of process. Values of \( \mu g \) around \( (1 + \Delta) / \epsilon \) (where \( \epsilon = 2.718 \ldots \) ) indicate first order kinetics and those around \( (1 + \Delta) / 2 \) indicate second order kinetics.

Another method using the value of \( \tau \) was given by Grosswienzer\(^{(20)} \) who found

\[ E = 1.51 k T_m T_1 / \tau \]  \hspace{1cm} (4.21)

which he claims to be accurate to better than \( \pm 5\% \). Dussel and Bube\(^{(21)} \) showed that Grosswienzer's method for \( E \) is out by about \( 7\% \).

Keating\(^{(22)} \) used the symmetry of the glow curve for evaluating the trap depth and gave the following formula for first order peaks.

\[ k T_m / E = (1.2 \gamma - 0.54) \omega / T_m + 0.0005 - \left[ \frac{1}{2} (\gamma - 0.75) \right]^2 \]  \hspace{1cm} (4.22)

from which \( E \) can be calculated where \( \gamma = \delta / \tau \).

Chen\(^{(23)} \) used a combination of theoretical and empirical-computational analysis to give corrected formulae for some of the previous methods. Apart from this he has developed a new method of calculating \( E \) by the use of the half width \( \omega \) and the maximum temperature \( T_m \). Chen's formulae for first and second order
kinetics are given below:

For first order kinetics

\[ E = 2.29 k \frac{T_m^2}{\omega} \quad (4.23) \]

and for second order kinetics

\[ E = 2k T_m \left( 1.756 \frac{T_m}{\omega} - 1 \right) \quad (4.24) \]

4.4 Analysis of complex TL glow patterns

For a single peak or well separated glow peaks, any of the formulae mentioned above can be used to calculate activation energy. In the case of complex TL curves exhibiting a number of overlapping glow maxima, some method of cleaning is necessary to analyse and separate the different glow peaks. Many methods of thermal cleaning (9, 24-26) have been suggested in which the phosphor is subjected to repeated cycles of heating. While applying the method of cleaning, it is expected however, that the phosphor should exhibit a reproducible glow pattern after undergoing continuous heat treatments. But an exact reproducibility is seldom achieved for most of the phosphors. It has been observed that deviations occur in positions of the glow maxima as well as in the intensity distribution of the different glow peaks. (25) Rao (27) has proposed a simple method of analysing the glow curves but the method does not deal with the cases where the glow peak maximum changes due to interference from the preceding peak.
Recently a modified analytical method for analysing the complex TL glow curves has been suggested by Khare and Ranade.\(^{(28)}\) Both the cases are discussed; the one in which glow peak maximum is affected and the other in which it remains unaffected by the neighbouring peak. By this method it has become possible to get well separated glow peaks and also to evaluate the trapping parameters to a better accuracy.

4.5 Experimental methods

The experimental techniques for the study of TL are essentially similar to those used for phosphorescence with an additional provision for heating the phosphor at a uniform rate and necessary arrangement for thermal insulation. In TL studies, uniform heating rate is an important parameter, as the theoretical analysis is based upon it. Low heating rate increases the resolution of glow curves,\(^{(29,30)}\) whereas a high heating rate gives rise to sharp maxima reducing the uncertainty in determining the temperature of maximum glow.\(^{(6,7)}\)

Apart from the heating rate, other factors such as accurate measurement of temperature, arrangements for low temperatures, protection of the phosphor from thermal radiation etc. are equally important.

Experimental arrangements used by some workers are mentioned below.

In the method of Randall and Wilkins\(^{(6)}\), a thin layer of
phosphor was spread on the surface of a copper box with the help of glycerol. An electric heater coil was arranged inside the box and a copper constantan thermocouple was soldered to the surface. Liquid air was used to get low temperature. The phosphor was excited by mercury arc and the glow intensity was measured with a photomultiplier and galvanometer. A further modification made by Garlick(31) makes it suitable to achieve a warming rate of $5^3K/sec$.

Bonfiglioli et al.(32) used a large copper plate with a small cavity at the centre to keep the sample. The temperature was measured with Pt/Pt -Rh thermocouple and the glow intensity was recorded directly on a photographic paper.

Hoogenstraten(3) coated the phosphor on the surface of a hollow cube made of chrome iron. The cube could be heated by an electric heating element kept inside; liquid nitrogen was used for cooling the cube. The measurement of temperature was done by silver-constantan thermocouple. The current from the photocell (IP 22) and thermocouple were fed via a microswitch to a single recorder, which recorded intensity and temperature as a function of time directly.

In another method Halperin et al.(19) mounted an alkali halide crystal in a vacuum cryostat which could be heated from liquid air temperature to $300^9K$. The radiation emitted by the crystal was received by a photomultiplier tube (IP 28) through a quartz window. After amplification the glow curve was recorded
FIG. 4.1 - THERMOLUMINESCENCE APPARATUS.
on a 50 mV Brown recorder. A copper constantan thermocouple was used to measure the temperature. The heating rate could be varied between 10 to 20°C per minute with an accuracy of about 0.2°C.

Shirowa et al. (5) varied the temperature of the sample from 77°C to 453°C. The phosphor was deposited in a layer on a plate attached to a copper rod. The lower half of the rod was mounted in a dewar flask containing liquid nitrogen. A nichrome wire was wound round this part of the copper rod to heat the sample. The output of the detector (IP 21) after proper amplification was recorded by a Sanborn (No. 154) recorder. A cam type programme controller was used to provide a constant heating rate of 0.25°C per second.

Recently Sanzelle and coworkers (33) have designed an apparatus for recording TL glow curves of various samples between 77°C and 773°C. It may also be used as a routine equipment for radiation dosimetry. Thermoluminescence of samples irradiated by α, β, γ rays or heavy ions can be studied.

4.6 Present method

For the present investigation, the apparatus has been designed in this laboratory and its description is given below.

(a) Apparatus: A schematic diagram of the apparatus used is shown in Fig. 4.1. It consists of a box O, made of copper sheets and the box is divided into two chambers. The lower
chamber B, has a long cylindrical cavity C, at the top for holding a metallic cup P to keep the phosphor. A heating element H made of Kanthal strip (20 ohms) is placed horizontally just below the cavity. The heating element is properly insulated with mica and its two ends are brought out of the chamber to terminals J and R. Two openings E and F provide inlet and outlet for air circulation. The upper part of the chamber A, has a side door I, to take the phosphor holder in and out. In the upper part, a slide assembly J is fixed at the top. This contains a hollow metallic cylinder K of the same diameter as the cavity. The top lid of the upper chamber has an opening to which a threaded metallic tube L is fixed for fitting the photomultiplier tube (IP 21). By sliding the plate J, the photomultiplier can be exposed to the phosphor or can be shielded from it.

In the present study, the source of excitation, the detector unit and the photomultiplier tube were the same as used in the emission study. The glow intensity was measured by an 'Inco spot reflection galvanometer' provided with four ranges. It has a coil resistance of 100 ohms and a sensitivity of 0.04 µA/ div. Zero adjusting device is provided to adjust the position of light spot on the scale. The arrangement for exciting the phosphor was made from outside the apparatus, because of the limitation of the size of the exciting source. The heating element was energized through a variac which was in turn connected to an A.C. voltage stabilizer.
FIG. 4.2 - CALIBRATION GRAPHS

- ○ C = 2.6 AMP., β = 1.0°K/SEC.
- ● C = 1.8 AMP., β = 0.5°K/SEC.
(b) Determination of phosphor temperature during heating:

In order to find the temperature of the phosphor at any time, the heater was calibrated. For this purpose, the cup A was filled with mercury and one junction of a copper-constantan thermocouple was immersed in it while the other junction was kept in ice. The current to be used in the final studies was passed through the heating element. A graph was plotted between the temperature and corresponding deflections of the galvanometer. Next, the deflection of galvanometer was noted as a function of time. With the help of these two graphs, a time versus temperature graph was obtained and from this the heating rate was determined. The calibration graph is shown in Fig. 4.2.

(c) Measurement of TL:

For glow measurements, the phosphor under investigation was filled up to a fixed mark in the cup A and was irradiated by X-rays (35 kV, 12 mA) for 4 minutes. During excitation, the intensity of the source and its distance from the phosphor were kept constant. The cup A was then placed in the TL apparatus and after shutting the side door, the plate J was pushed inside so that the cylinder K comes just in line with the phosphor and the photomultiplier tube. The phosphor was allowed to decay till the intensity reduced to a very low value. The heater current was switched on and the galvanometer deflection was noted as a function of time. The glow curve was then plotted with the help of the
FIG. 4.3(a) -- GLOW CURVES OF CaS:Eu PHOSPHORS.
FIG. 4.3(b) - GLOW CURVES OF CaS: Tb PHOSPHORS
FIG. 4.3 (c) - GLOW CURVES OF CaS: (Eu 0.1%, Tb) PHOSPHORESCENCE

HEATING RATE °K/SEC

TEMPERATURE, °K

INTENSITY, Unit a.

R1, R2, R3, R5, R6
FIG. 4.3(d) - GLOW CURVES OF CaS: (Tb 0.1, Eux) PHOSPHORS
calibration graph. In this way all the samples were studied at the heating rates of 1°K/sec. and 0.5°K/sec. in the temperature range of 300° to 500°K.

4.7 Results

(a) Glow curves: The glow curve for the phosphors of different series at the heating rate of 1°K/sec. are shown in Figs. 4.3 (a) – (d). Only one peak appears for all the samples. For comparison the samples have been studied at a lower heating rate of 0.5°K/sec. as well. With change in heating rate there is no apparent change in general shape of the glow curves except that glow peak maxima have shifted towards low temperatures.

At the higher heating rate the glow curves show sharp maxima and increase in peak intensity. The lower heating rate did not produce any further resolution nor indicate any complex glow pattern.

In the first two series, viz., CaS : Eu and CaS : Tb, the glow peak intensity increases with the increase of activator up to an optimum concentration before decreasing, the glow peak maxima remaining practically unaffected. In the series CaS : ( Eu 0.1, Tb x ) the intensity of the glow peak increases with addition of Tb up to an optimum value before decreasing. On the other hand in the case of CaS : ( Tb 0.1, Eu x ) the intensity decreases continuously as the amount of Eu is increased. The glow peak maxima and
the shape (having only one peak) remain unaltered. It appears, therefore, that there is only one group of traps in the present phosphor system within the temperature range studied.

In order to know the kinetics involved the values of shape factor, \( \mu_g = \delta / \omega \) have been calculated. The results are shown in Tables 4.2 and 4.3. For most of the phosphors the value of \( \mu_g \) is found to lie between 0.50 and 0.54; in a few cases \( \mu_g \) is less than 0.50 but is always greater than 0.44. This indicates the predominance of second order kinetics as Chen's value of \( \mu_g \) for second order is 0.52 \( \pm \) 0.02. (23)

(b) Trap depth : From the glow curves obtained at both the heating rates, trap depths have been calculated using Curie's formula:

\[
E (\text{eV}) = \frac{T_m (0K) - T_o (\beta / S)}{\Theta (\beta / S)}
\]

where the symbols have already been explained. Using the data given in Table 4.1 graphs were plotted between \( T_o \) and \( \beta / S \) as well as between \( \Theta \) and \( \beta / S \). From the graph the values of \( T_o \) and \( \Theta \) were obtained for the two values of \( \beta / S \), where \( \beta \) is the heating rate (10 K/sec. and 0.50 K/sec.) and \( S \) is taken to be \( 10^9 \) per second, which is the value suggested by Randall and Wilkins (6) for sulphide phosphors and which has also been used by other workers. (34, 35)

Thus the formulae for trap depth become :
FIG. 44(a) - TL OF CaS: Eu (0.05 MOLE %)
For the higher heating rate \( \beta_1 = 1^\circ K/sec. \)

\[
E \ (eV) = \frac{T_m \ (^\circ K) - 10}{480}
\]

For the lower heating rate \( \beta_2 = 0.5^\circ K/sec. \)

\[
E \ (eV) = \frac{T_m \ (^\circ K) - 8.5}{460}
\]

The glow peak temperatures, shape factors and the trap depths thus calculated are given in Tables 4.2 and 4.3. For both the heating rates the values of trap depths are nearly the same. Further there is no regular variation of \( E \) with the activator concentration. The value of \( E \) lies between 0.74 and 0.78 eV.

(c) Colour of TL : To ascertain the colour of TL, the experimental set up described in Chapter III was used.

In the emission study of the samples, it has been observed that CaS : Eu phosphor gives a broad band emission with peak wavelength at 640 nm and CaS : Tb phosphor gives line emission with seven distinct peaks. Hence to verify the colour of TL, the drum of the B.S. spectrometer was set first at 640 nm and the thermoluminescence of CaS : Eu phosphor was recorded by photometer. The glow curve so obtained resembles closely with that recorded by taking the total light sum from the same sample Fig.4.4(a).
FIG. 44(b) - TL OF CaS: Tb (0.1 MOLE %)
Similarly for CaS : Tb phosphor, two lines were selected: the one at 550 nm originating from $5D_4$ level and the other at 437 nm originating from $5D_3$ level of terbium. The spectrometer was set at these two wavelengths separately, and the glow curves were recorded by photometer. The glow curve so obtained may be compared with that obtained by taking the total light sum Fig. 4.4(b). A close agreement between the TL curves as regards shape and glow peak maximum, reveals that the colour of TL emitted by these samples (CaS : Eu and CaS : Tb) is the characteristic colour of europium and terbium emissions respectively.
Table 4.1

Quoted from D. Curie's 'Luminescence in Crystals'. Methuen & Co., Ltd., London, p. 162 (1963)

<table>
<thead>
<tr>
<th>$\beta / S \ (^\circ K)$</th>
<th>$\Theta \ (^\circ K / eV)$</th>
<th>$T_0 \ (^\circ K)$</th>
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<td>$10^{-5}$</td>
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<td>$10^{-14}$</td>
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Table 4.2

Glow peak parameters at $\beta = 1^\circ K/\text{sec.}$

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$T_m$ (°K)</th>
<th>$E$ (eV)</th>
<th>$\mu g = E/\omega$</th>
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<tr>
<td>$E_1$</td>
<td>376</td>
<td>0.76</td>
<td>0.45</td>
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<tr>
<td>$E_2$</td>
<td>381</td>
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<td>$E_3$</td>
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<td>$E_4$</td>
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<td>0.50</td>
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<td>$E_5$</td>
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<tr>
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<td>0.51</td>
</tr>
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<td>0.51</td>
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<td>375</td>
<td>0.76</td>
<td>0.51</td>
</tr>
<tr>
<td>$T_5$</td>
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<td>0.74</td>
<td>0.54</td>
</tr>
<tr>
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<td>0.47</td>
</tr>
<tr>
<td>$N_5$</td>
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<td>0.75</td>
<td>0.48</td>
</tr>
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</table>
Table 4.3

Glow peak parameters at $\beta = 0.5^\circ$K/sec.

<table>
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<th>$T_m$ (°K)</th>
<th>$E$ (eV)</th>
<th>$\mu g = \delta / \omega$</th>
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