mined by the temperature of the annealing – a proposition featuring in the literature [8] – as comparison of points 4 and 5 and of points 6 and 7 will show. Both of the above inferences are clearly in conflict with existing views based on investigations along different lines. Without independent crystallinity measurements, not carried out at the time of the X-ray studies, the issue cannot be profitably discussed any further. Nevertheless, in the conviction that the results are real we thought it appropriate to place them on record.

References

1. H. G. THIELKE and F. W. BILLMEYER, *J. Polymer Sci. A* **2** (1964) 2947.
2. W. O. STATTON, in "Newer Methods of Polymer Characterization", edited by B. Ke (Interscience, New York, 1964) Chapter 6.
3. Y. KOBAYASHI and A. KELLER, *Polymer* **11** (1970) 114.
4. A. H. WINDLE, *J. Mater. Sci.* **10** (1975) to be published.
5. F. W. JONES, *Proc. Roy. Soc. A* **166** (1938) 16.
6. W. H. BRAGG and W. L. BRAGG, "The Crystalline State, I. General Survey" (G. Bell and Sons, London, 1933) p. 189.
7. W. WILKE, W. VOGEL and R. HOSEMANN, *Kolloid Z. u. Z. Polymere* **237** (1970) 317,
8. E. W. FISCHER, *Faserforsch. Text. Tech.* **15** (1964) 545.

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Comment on a paper by Ziniker, Rusin and Stoebe

In a recent study of thermoluminescent peaks in Al_2O_3, MgO and LiF (TLD-100) Ziniker *et al.* [6] discuss the variation in reported values of the activation energies obtained for each peak. They conclude that the energies obtained are related to the method of measurement, the most reliable for a first order peak being the isothermal decay method.

Whilst studying the thermoluminescent peaks in a quartz which had been used for archaeological dating (Aitken and Fleming, [1]), I found a similar discrepancy and was able to show that it could be attributed to the occurrence of thermal quenching [5]. Three methods of measuring the activation energy E for the 325°C peak were used:

(a) the isothermal decay method which gave $E = 1.7 \pm 0.1$ eV

(b) Hoogenstraaten's method [5], where the variation of peak temperature T_m with heating rate β is obtained and the slope of log T_m^2/β versus T_m^{-1} yielded $E = 1.69 \pm 0.02$ eV.

(c) the initial rise method which gave $E = 1.05 \pm 0.03$ eV.

Methods (a) and (b) can only be applied to a first order peak; the initial rise method is generally accepted to be the most widely applicable since the initial part of the glow curve is independent of the kinetics of trap emptying (Kelly and Bräunlich, [4]). This method assumes that the initial part of the glow curve obeys the relation

$$I = Cf(n)\exp(-E/kT)$$

where $f(n)$ represents the kinetics of trap emptying and C is related to the luminescence efficiency. Hence this method relies on the constancy of the luminescence efficiency, a point which is usually overlooked.

Now the luminescence efficiency of a phosphor may be expressed as the ratio

$$\eta(T) = \frac{P_r}{P_r + P_{nr}}$$

where P_r is the probability of radiative emission, assumed independent of temperature, and P_{nr} is the probability of a non-radiative transition, which rises with increasing temperature. The resulting decrease of η with temperature rise is known as thermal quenching (Curie).

If only one type of luminescence centre is present we have

$$\eta(T) = \frac{1}{1 + K\exp(-W/kT)}$$

where W is an energy depth characterizing the non-radiative process and K is a constant, and thus for $K\exp(-W/kT) \gg 1$, $\eta(T) \approx K^{-1}$

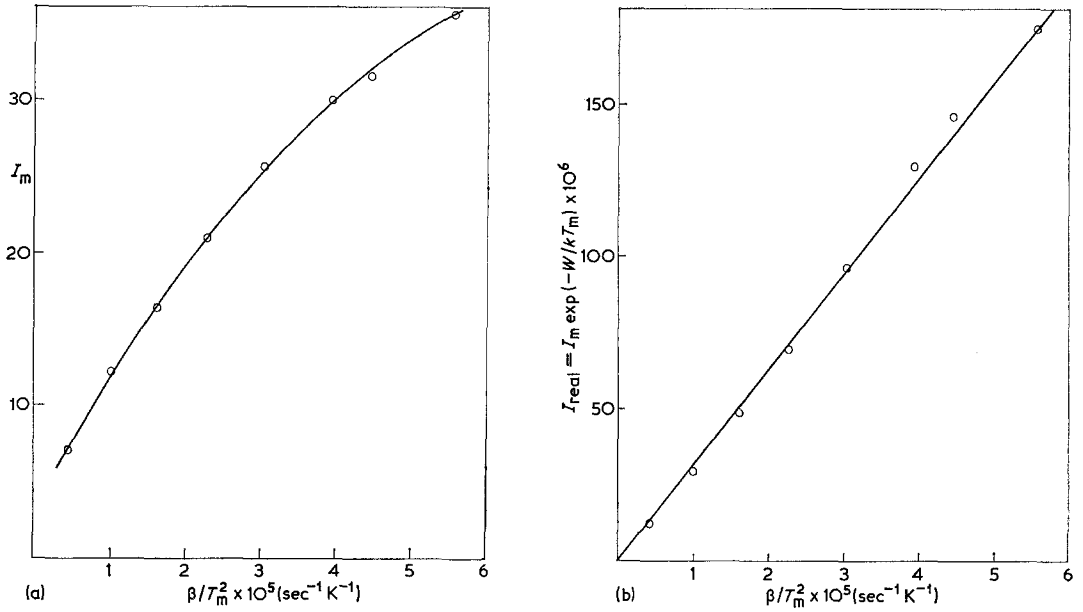

Figure 1(a) 325°C quartz glow peak: peak intensity I_m versus β/T_m^2. (b) I_m exp(− W/kT) versus β/T_m^2.

exp(W/kT). This suggests that a better expression for the initial part of the glow curve is

$$I \propto \exp[(W - E)/kT]$$

and hence that if thermal quenching is occurring, then the values of E derived by the initial rise method will be too small by an amount W.

The presence of thermal quenching was demonstrated by observation of the prompt luminescence observed as a function of temperature during irradiation. The value of W thus obtained was the same as the discrepancy in the two values of E obtained by the different methods.

Thermal quenching can also be observed by the departure from linearity of the plot of the peak intensity I_m versus β/T_m^2 for the same initial irradiation, illustrated in Fig. 1a for the 325°C peak in quartz. If however I_m exp(− W/kT_m) is plotted instead, as in Fig. 1b, the result is a straight line passing through the origin.

In summary, the presence of thermal quenching invalidates the initial rise method for determining the thermal activation energy, causing it to yield results that are too small.

References

1. M. J. AITKEN and S. J. FLEMING, Thermoluminescence dosimetry in archaeological dating, in "Topics in Radiation Dosimetry" supplement 1 (edited by F. H. Attix) (Academic Press, 1, 1972).
2. D. CURIE, "Luminescence in Crystals" (Wiley, New York, 1963).
3. W. HOOGENSTRAATEN, *Philips Res. Rep.* **13** (1958) 515.
4. P. KELLY and P. BRÄUNLICH, *Phys. Rev. B*, **1** (1970) 1587.
5. A. G. WINTLE, Unpublished D.Phil. Thesis, Oxford University, 1974.
6. W. M. ZINIKER, J. M. RUSIN and T. G. STOEBE, *J. Mater. Sci.* **8** (1973) 407.

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