JOURNAL OF MATERIALS SCIENCE 7 (1972) 1465-1471

Review: a review of the recent methods for determining trap depth from glow curves

C. S. SHALGAONKAR, A. V. NARLIKAR
Materials Research Laboratory, Department of Physics, Shivaji University, Kolhapur, India

The paper reviews some of the important methods used in determination of the trap depth E from glow curves. Their suitability, merits and demerits are examined.

1. Introduction

It is now well established that the electronic processes in the materials are markedly influenced by the presence of trapping levels. However, because of numerous complexities involved in real materials, a detailed quantitative theory of electron traps is still lacking. Attempts made so far in this direction have been confined to simple cases under certain specific assumptions. Most of the information presently available on real materials has been derived mainly from experimentation. For such studies, fluorescent materials have attracted a particular interest because their remarkable properties are mainly due to the electron traps. The experimental measurements have proved invaluable in providing a direct insight into the electronic process involved and have yielded valuable information about trapping levels.

The most important parameter to be determined is E, the trap depth which is nothing but the thermal energy required to liberate a trapped electron. There are several methods proposed for determining E. However, the experiments which have proved most convenient are the measurements of thermally stimulated luminescence (TSL) and thermally stimulated conductivity (TSC). In TSL, the sample is first excited optically in dark and is then warmed up at a linear heating rate. The resulting luminescence intensity is measured as a function of the sample temperature. The curve obtained showing a variation of intensity with temperature is referred to as the "glow curve". In TSC, on the other hand, the electrical conductivity is studied as a function of temperature. If required both these measurements can be performed simultaneously.

The theory of TSL can be applicable with slight modification to the TSC case. Here the conductivity is related to the glow intensity I by the relation $\sigma = \tau e \mu I$, where τ is the life time, e is the charge, μ is the mobility.

Several methods based on the analyses of the glow curves and TSC curves have been proposed and used for determining E, and they are reviewed in this paper. The attempts have been made to determine E from other related properties such as the dielectric constant and the photoluminescence decay, but such methods are not discussed in the present review.

2. Determination of the trap depth

A typical glow curve exhibiting a single peak is shown in Fig. 1. Temperature corresponding to the maximum intensity is called the peak temperature T_m. Variation in the temperature range can result in more peaks, each corresponding to a specific trap depth. In the case of overlap, the successive peaks can be distinguished by suitably quenching the previous peaks. The individual peaks can be analysed in numerous ways and E can be determined. The methods can be categorized in three main types: (1) methods based on T_m, (2) methods based on the shape of the curve, and (3) methods based on both T_m and the shape.

2.1. Methods based on T_m

2.1.1. Method due to Randall and Wilkins

The first theoretical treatment for a well-isolated thermoluminescence peak has been due to Randall and Wilkins [1]. Their analysis is based on a model in which there are a number of discrete trapping levels from which electrons are thermally excited into the conduction band, and the recombination of free electrons takes place at

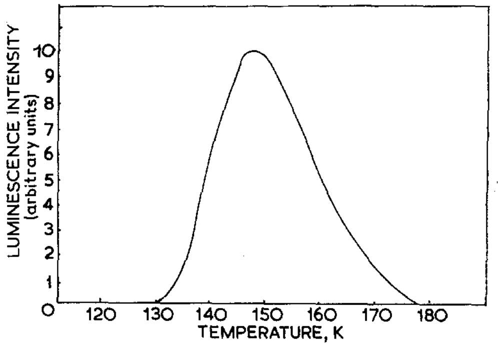

Figure 1 A typical glow curve showing single glow peak.

deep centres. The theory makes the following three assumptions: (a) glow peaks corresponding to different trapping levels do not overlap, (b) transitions directly between various trapping states and other centres are negligible, and (c) the life-time τ for recombination is so small that $(\mathrm{d}n)/\mathrm{d}t \ll n/\tau$ where n is the concentration of electron in the conduction band, an assumption, in general, found to be true for phosphors and semiconductors.

The electrons in traps have Maxwellian distribution of thermal energies, and hence one can write

$$\frac{\mathrm{d}n}{\mathrm{d}t} = nS \exp\left(-\frac{E}{kT}\right) \tag{1}$$

where S is the escape frequency factor or the pre-exponential factor as it is also sometimes called. The solution of Equation 1 is given by

$$n = n_0 \exp\left[\left(-\frac{S}{\beta}\right)\int_{T_0}^{T} \exp(-E/kT)\,\mathrm{d}T\right] \tag{2}$$

where n_0 is the initial concentration of trapped electrons prior to heating, and β is the heating rate. The intensity I of the thermoluminescence peak is given by

$$I = -C\frac{\mathrm{d}n}{\mathrm{d}t} = C n_0 S \exp\left(-\frac{E}{kT}\right)$$
$$\exp\left[\left(-\frac{S}{\beta}\right)\int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right)\mathrm{d}T\right] \tag{3}$$

where C is a constant of proportionality. In the beginning, the intensity rises exponentially with temperature. However, soon the concentration of trapped electron is considerably reduced and the intensity, after reaching a maximum at a certain temperature T_m, begins to fall and reaches to zero when all the traps have emptied. In the Randall and Wilkins method, T_m corresponds to temperature a little below which the frequency of an electron escaping the trap is 1 per second, that is

$$S \exp\left(-\frac{E}{kT_\mathrm{m}}\right) \times \{1 + f(S, \beta)\} = 1$$

The function $f(S, \beta) \ll 1$, and this gives the trap depth E

$$E = T_\mathrm{m}[1 + F(S, \beta)]\, k \log S \tag{4}$$

where $F(S, \beta)$ is another function of S and β. For $S = 2.9 \times 10^9\ \mathrm{sec}^{-1}$ the above relation reduces to

$$E = 25kT_\mathrm{m} \tag{5}$$

This is very similar to the relation given independently by Urbach [2], also derived from Equation 3, for $S \approx 10^9\ \mathrm{sec}^{-1}$

$$E = T_\mathrm{m}/500 \tag{6}$$

Both Equations 5 and 6 are found to yield a right order of magnitude of E for a number of phosphors [3, 4]. The numerical factors in both equations are dependent upon the value of S, and hence, the values of E thus obtained are only approximate. S, in fact, may be different for each trap in the same substance.

The position of maximum is obtained by differentiating Equation 3 with respect to T and equating to zero which yields

$$\frac{E}{kT_\mathrm{m}^2} = \frac{S}{\beta}\exp\left(-\frac{E}{kT_\mathrm{m}}\right) \tag{7}$$

The above equation can be evaluated numerically and within an error of 1% it can be expressed [5] as

$$E = \frac{T_\mathrm{m}(K) - T_0(\beta/S)}{K(\beta/S)} \tag{8}$$

where the functions T_0 and K may be obtained graphically for different values of β/S and then used for determining E [4, 6, 7]. If either of the parameters E and S are known the Equation 7 can serve as a transcendental equation which can be solved numerically for the unknown parameter. However, as there are several other methods to determine E, which do not require the knowledge of S, the Equation 7 is invariably used for determining the parameter S.

2.1.2. Method due to Booth and Bohun

The method suggested independently by Booth [8] and Bohun [9] uses different heating rates to estimate E. Solving Equation 7 for two different heating rates β_1 and β_2 they find

$$E = \frac{k\, T_{m_1} T_{m_2}}{T_{m_1} - T_{m_2}} \log \frac{\beta_1 T_{m_2}^2}{\beta_2 T_{m_1}^2} \qquad (9)$$

where T_{m_1} and T_{m_2} are respectively observed peak temperatures corresponding to heating rates β_1 and β_2. S is given by [10]

$$\log \frac{Sk}{E} = \left[T_{m_2} \log \frac{T_{m_2}^2}{\beta_2} - T_{m_1} \log \frac{T_{m_1}^2}{\beta_1} \right] \Big/ (T_{m_1} - T_{m_2}) \qquad (10)$$

This method is convenient for determining E. If T_m can be measured within an accuracy of 1 K the method is found to yield E within 5%. Schon [11] has modified the equation by replacing T_m^2 by $T_m^{3.5}$ which has resulted in somewhat improved accuracy.

2.1.3. Method due to Hoogenstraaten

Another method for measuring E is due to Hoogenstraaten [12] who, using Equation 7 has shown that peak temperature is related to E by the equation

$$\log (T_m^2/\beta) = \frac{E}{kT_m} + \log \frac{Sk}{E} \qquad (11)$$

Thus the plot between $\log (T_m^2/\beta)$ against $1/T_m$ is linear having a slope E/k and intercept $\log Sk/E$. Thus both E and S can be determined [13]. Apart from being simple the method has the advantage of being insensitive to retrapping effects.

2.2. Methods based on the shape of the curve

2.2.1. Initial rise method

This method is due to Garlick and Gibson [14] and is an extension of Randall and Wilkins' theory. For the second order kinetics they find

$$I = n_0^2\, S \exp\left(-\frac{E}{kT}\right) \Big/ N \left\{ 1 + \frac{n_0}{N} \int_{T_0}^{T} \frac{S}{\beta} \exp\left(-\frac{E}{kT}\right) \mathrm{d}T \right\}^2 \qquad (12)$$

This equation is equivalent to Equation 3 applicable to the first order kinetics. In the temperature range $T < T_m$ all the factors other than $\exp(-E/kT)$ in both Equations 3 and 12 do not vary much and, therefore, in the initial part of the glow curve $I \propto \exp(-E/kT)$ for either type of kinetics. Thus, the plots of $\log I$ against $1/T$ are linear having slope equal to $-(E/k)$. This provides a quick analysis of the initial ascending part of the glow peak which yields the value of E without any knowledge of S [3, 15]. However, due to some experimental [16] and theoretical [17, 18] reasons under certain situations, the method is found to be inconsistent.

2.2.2. Isothermal decay method

In this method, after excitation, the sample is quickly heated to a specific temperature and at this temperature the luminescence decay is measured. The method, being isothermal, has the advantage that such difficulties, as arising from overlapping peaks and change in quantum efficiency or the emission spectra occurring under the non-isothermal conditions, are avoided. The decay curve obtained can be analysed and it has been shown [19] that for the first order kinetics,

$$I(T) = n_0 S \exp\left(-\frac{E}{kT}\right) \exp\left[-St \exp\left(-\frac{E}{kT}\right)\right] \qquad (13)$$

giving

$$\log I(T) = -St \exp\left(-\frac{E}{kT}\right) - \frac{E}{kT} + \log(n_0 S) \qquad (14)$$

The slope of the linear plot obtained between $\log I(T)$ against t is

$$m = S \exp\left(-\frac{E}{kT}\right) \qquad (15)$$

Taking the slopes m_1 and m_2 at two temperatures T_1 and T_2 give

$$\log \frac{m_1}{m_2} = \left[\frac{1}{T_1} - \frac{1}{T_2}\right]\left(-\frac{E}{k}\right) \qquad (16)$$

From Equations 15 and 16 the value of E and S can be determined [3].

2.3. Methods depending on both shape and T_m

There have been several methods proposed which use the peak temperature T_m and two temperatures T_1 and T_2 which are respectively the temperatures on either side of T_m corresponding to half the intensity (Fig. 2). T_1 and T_2 depend upon the shape of the glow curve.

2.3.1. Grossweiner's method

Using Equation 3 for the first order kinetics, Grossweiner [20] has shown that E, in terms of T_m and T_1, is given by

$$E = 1.51\, k\, T_m T_1/(T_m - T_1) \qquad (17)$$

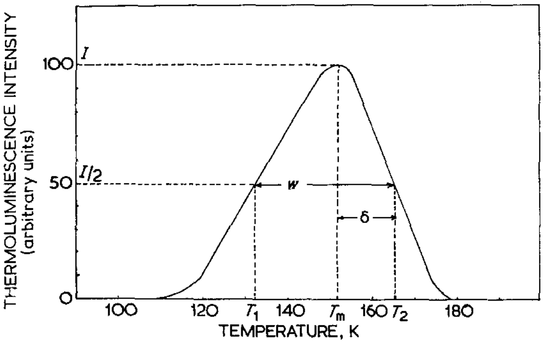

Figure 2 Different parameters determining the shape of the glow curve.

E thus calculated is found to be accurate within $\pm$ 5% provided $S/\beta > 10^7$ deg^{-1} and $E/kT_m > 20$ [13]. The above formula is empirically modified by Chen [21] with 1.41 replacing 1.51. This yields E with a better accuracy.

2.3.2. *Method due to Lushchik*

Results very similar to above have been obtained by Lushchik [22]. For the first order kinetics, he has obtained

$$E = k\, T_m^2/(T_2 - T_m) \tag{18}$$

The derivation is on the assumption that the area of the peak towards the fall-off is equal to the area of the triangle having the same height and half width, an assumption which is found true for an accuracy of 5%. Under this assumption, for the second order kinetics E is given by

$$E = 2k\, T_m^2/(T_2 - T_m) \tag{19}$$

The merit of Grossweiner and Lushchik methods is in their obvious simplicity in evaluating E [13]. For better accuracy, the above two equations have been empirically modified by Chen [21] by multiplying by 0.978 and 0.853 for the first and second order kinetics respectively.

2.3.3. *Halperin and Braner's method*

A somewhat different approach which uses both T_1 and T_2 is due to Halperin and Braner [23]. They considered luminescence emission as mainly due to two kinds of recombination processes. In one process the recombination takes place via conduction band and in the other the electron raised to an excited state within the forbidden gap below the conduction band recombines with the hole by tunnelling process. In the first type of process the value of E is found to be

$$E = q\, k\, T_m^2\,(1 - \Delta)/(T_2 - T_m) \tag{20}$$

while in the other it is given by

$$E = q\, k\, T_m^2/(T_2 - T_m) \tag{21}$$

where $\Delta = 2k\,T_m/E$, and q depends upon the shape of the glow peak and the kinetics of the process. For the first and second order kinetics q is respectively given by

$$q_1 = [1.72\, \mu_g/(1 - \mu_g)]\,(- 1.58\Delta)$$
$$q_2 = [2\, \mu_g/(1 - \mu_g)]\,(1 - 2\Delta)$$

where $\mu_g = (T_2 - T_m)/T_m - T_1$ is the symmetry factor which is a convenient parameter to decide the type of kinetics involved. If $\mu_g < e^{-1}(1 + \Delta)$ the kinetics is of first order while $\mu_g \geqslant e^{-1}(1 + \Delta)$ corresponds to the second order kinetics. On substituting the values of q in Equations 20 and 21 for E and calling $T_m - T_1 = \tau$ yields E for two types of kinetics

$$E_1 = (1.72/\tau)\, k\, T_m^2\,(1 - 2.58\Delta) \tag{22}$$
$$E_2 = (2/\tau)\, k\, T_m^2\,(1 - 3\Delta) \tag{23}$$

Here expressions containing higher powers of Δ are neglected. The advantage of this method is that the first half of the peak is sufficient for the evaluation of E, and it also points a way of determining the kinetics of the process involved [24, 4].

2.3.4. *Method due to Chen*

The method suggested by Chen [21] to determine E follows from Randall-Wilkins' formula with the same assumption as of Lushchik. For the first order kinetics E is given by

$$E_1 = 2k\, T_m[1.25\, T_m/(T_2 - T_1 - 1) \tag{24}$$

and for second order kinetics

$$E_2 = 2k\, T_m[1.756\, T_m/(T_2 - T_1 - 1) \tag{25}$$

In the above equations, the numerical constants are chosen empirically to give a good estimation of E.

2.3.5. *Keating method*

The methods described so far assume S, the frequency factor, to be independent of temperature. There is, however, substantial evidence [25, 26] to suggest the assumption to be unjustified. Keating [27], thus considered $S = \mathrm{B}T^a$ where B is a constant, and the magnitude of a is given by $-2 \leqslant a \leqslant +2$. For the first order kinetics the final expression for E is found to be

$$E = k\, T_m \left\{(1.2\Gamma - 0.54)\left(\frac{T_2 - T_1}{T_m}\right) + 0.0055 - [\tfrac{1}{2}(\Gamma - 0.75)]^2\right\}^{-1} \tag{26}$$

where $\Gamma = T_2 - T_m/T_m - T_1$, and T_1 and T_2 being defined earlier. The formula is found to hold true for $0.75 < \Gamma < 0.9$ and $10 < E/k\,T_m < 35$ [13].

2.3.6. *Inflection point method*

In this method, suggested by Land [28], use is made of the inflection temperature T_i of the glow curve for evaluating E. The inflection temperature is given by setting the second derivative for the intensity temperature relation expressed by Equation 3, to zero. This gives

$$E = \frac{k\,T_m\,T_i}{|T_i - T_m|} \log A/Q \qquad (27)$$

where $Q = (T_i/T_m)^2$ and $A = 0.77$ and 2.66 respectively for $T_i < T_m$ and $T_i > T_m$. Thus, by measuring T_i and T_m, E can be determined. The method has been applied for evaluating E for Y_2O_3 and ThO_2. Except when the peaks are overlapping, the method has yielded consistent results.

2.3.7. *Numerical kinetics method*

This method of analysis [29] involves a numerical computation which proceeds in small arbitrary time steps. During each step the concentration of trapped charge, the carrier concentrations, the radiative relaxations of excited centres, etc. are adjusted in accordance with the physical processes involved. When used to analyse the experimental data some initial approximate values of E and S are chosen and they are suitably varied to determine the values giving the best least-square fit to the experimental data.

2.3.8. *Area measurement method*

The method proposed by Muntoni *et al* [30] for activation energy is based on the area under the glow curve. The kinetic equation proposed by Antonov-Romanovskii [31] and Lushchik [32] is of the form

$$-\frac{dm}{dt} = A\,m^{\alpha}\,e^{-E/KT} \text{ giving } I = -\alpha\beta\,\frac{dm}{dT} \qquad (28)$$

where α is a suitable numerical parameter representing kinetics order. On integration, the above equation takes the form $m(T) = S(T)/\alpha/3$ where $S(T)$ is the integrated area of the curve in the interval from T to T_f where T_f is the temperature corresponding to the end of the glow curve. The above equation may be expressed

$$\log\frac{1}{[S(T)]^{\alpha}} = \frac{E}{k\,T_m} + C \qquad (29)$$

where $C = \log(A\,\alpha^{1-\alpha}\,\beta^{\alpha})$. Plot of $\log[1/S(T)^{\alpha}]$ versus $1/T$ gives straight line, slope of which determines the activation energy.

If in the case of bimolecular process, where $\alpha = 2$, the curve is concave while for the monomolecular case, where $\alpha = 1$, the curve is convex, the value of α which results in linear plot represents the order of kinetics involved. In general, α may be fractional. The method thus provides a semiempirical approach to thermoluminescence.

Another method involving area measurement is suggested by Maxia *et al* [33] who have shown that

$$\log\left\{I(T)\,\frac{\cos\theta + \sin\theta\,S(T)}{S^2(T) + \Delta\,S(T)}\right\} = -\frac{E}{kT} + \mu \qquad (30)$$

or

$$Y = -\frac{EX}{k} + \mu \qquad (31)$$

where Y is the term on the left hand side and $X = 1/T$. θ is a function of the area of the glow curve and probability factors for recombination and retrapping which determines the linear behaviour of Y and X. Except for θ all quantities on the left hand side of the above equation can be determined from the TL spectrum.

The correlation coefficient

$$\rho = \frac{\mathrm{cov}(X, Y)}{[V(X)\,V(Y)]^{\frac{1}{2}}}$$

can be numerically computed as a function of θ, and θ is conditioned for ρ or ρ^2 attaining unity. From this the activation energy is given by

$$E = -k\,\frac{\mathrm{cov}(X, Y)}{V(X)} = -k\,\frac{\mathrm{cov}(X, Y)}{V(Y)} \qquad (32)$$

E calculated thus is found to agree with that obtained using the method of Muntoni *et al* [30].

3. Conclusion

Having reviewed above various methods used for determining the trap depth E it is now worth examining briefly their points of merits and demerits. Although such points were mentioned in the preceding sections while considering the individual methods it seems appropriate to summarize them here.

The methods belonging to the first category, that is, those based on T_m alone, have the common drawback that they assume the monomolecular kinetics in the luminescence process. Thus, unless one is sure that it is not really justifiable to use them for evaluating E, the same criticism should be applied to the isothermal decay method of the second category, and Grossweiner's and Keating's methods of the third category. The initial rise method described in Section 2.2.1 is, on the other hand, based on the measurements carried out in the lower part of the low temperature side of the glow peak which are affected least by the type of kinetics, and hence, the method is independent of the kinetics involved. As would be expected, the values of E thus calculated are however associated with traps which are relatively shallow.

When the kinetics are not known E is most reliably determined using the methods of the third category, excepting the two methods mentioned above. Of these, Halperin and Braner's method and the area measurement method described respectively in Sections 2.3.3 and 2.3.8 are particularly convenient for determining the type of kinetics involved. Once the kinetics are known a good estimate of E can be obtained using various methods such as of Lushchik and Grossweiner, incorporating the empirical modifications suggested by Chen.

Despite the analytical and experimental simplicity of the TSL it is worth pointing out some of its obvious limitations. First of all the experimental arrangement is, in general, such that the method possesses a degree of uncertainty in the actual temperature of the sample. There is a temperature gradient between the lower and upper surface of the sample. This can be reduced by using thin and flat-faced samples.

Another drawback of TSL is that when the trapping levels are close together the glow peaks tend to overlap and the problem of resolution of the individual peaks becomes formidable. In the case of overlap, the individual peaks can, in general, be isolated by suitably quenching the previous peaks. Nevertheless, the method still leaves uncertainties in the resolution of the peaks.

Further criticism of TSL is that the measurements are sensitive to structural inhomogeneities. Results obtained on single crystals are, in general, found to differ from those obtained on polycrystalline or powdered samples of the same material. Also, surface states can produce peaks on the glow curve which are found to vary with the irradiation dose. This can affect the shape of the original glow curve and make the problem of peak resolution difficult. Lastly, TSL cannot detect the non-radiative centres. This can, however, be done by TSC studies.

Acknowledgement

The authors are indebted to Professor D. R. Bhawalkar of the University of Saugar for encouragement and discussions, and they are grateful to their colleagues Mr S. H. Pawar and Mr R. D. Lawangar for going through the manuscript and making valuable suggestions.

References

1. J. T. RANDALL and M. H. F. WILKINS, *Proc. Roy. Soc.* **A184** (1945) 366.
2. F. URBACH, Cornell Symposium (Wiley, New York, 1946) 115.
3. P. D. TOWNSEND, C. D. CLARK, and P. W. LEVY, *Phys. Rev.* **155** (1967) 908.
4. S. H. PAWAR, R. D. LAWANGAR, C. S. SHALGAONKAR, and A. V. NARLIKAR, *Phil. Mag.* **24** (1971) 727.
5. D. CURIE, "Luminescence in Crystals" (Methuen, London, 1963) 162.
6. D. SHARMA and A. SINGH, *Ind. J. Pure and Appl. Phys.* **7** (1969) 310.
7. B. R. MALHOTRA, Ph.D. Thesis, University of Saugar (1968).
8. A. H. BOOTH, *Canad. J. Chem.* **32** (1954) 214.
9. A. BOHUN, *Czech. J. Phys.* **4** (1954) 91.
10. A. WREZESINSKA, *Acta Phys. Polonica* **15** (1956) 151.
11. M. SCHON, *Tech-Wiss Abhand Osram-Ges.* **7** (1958) 175.
12. W. HOOGENSTRAATEN, *Philips Res. Reports*, **13** (1958) 515.
13. K. H. NIØCHOLAS and J. WOODS, *Brit. J. Appl. Phys.* **15** (1964) 783.
14. G. F. J. GARLICK and A. F. GIBSON, *Proc. Phys. Soc.* **60** (1948) 574.
15. A. HALPERIN, A. A. BRANER, A. BEN-ZVI, and N. KRISTIANPOLLER, *Phys. Rev.* **117** (1960) 416.
16. J. HAAKE, *J. Opt. Soc. Amer.* **47** (1957) 649.
17. F. ARAMU, P. BROVETTO, and A. RUCCI, *Phys. Letters* **23** (1966) 308.
18. P. BRAUNLICH, *J. Appl. Phys.* **38** (1967) 649.
19. G. F. J. GARLICK, "Luminescent Materials" (Oxford University Press, New York, 1949).
20. L. I. GROSSWEINER, *J. Appl. Phys.* **24** (1953) 1306.
21. R. CHEN, *ibid* **40** (1969) 570.
22. C. B. LUSHCHIK, *Soviet Phys. JETP* **3** (1956) 390.
23. A. HALPERIN and A. A. BRANER, *Phys. Rev.* **117** (1960) 408.
24. C. BETTINALI, G. FERRARESSO, and J. W. MANCONI, *J. Chem. Phys.* **50** (1969) 3957.
25. M. LAX, *Phys. Rev.* **119** (1960) 1502.
26. G. BEMSKI, *ibid* **111** (1958) 1515.
27. P. N. KEATING, *Proc. Phys. Soc.* **78** (1961) 1408.
28. P. L. LAND, *J. Phys. Chem. Solids* **30** (1969) 1681.

29. P. J. CHEMMY, P. D. TOWNSEND, and P. W. LEVY, *Phys. Rev.* **155** (1967) 917.
30. C. MUNTONI, A. RUCCI, and A. SERPI, *Ricerca Sci.* **38** (1968) 762.
31. V. V. ANTONOV-ROMANOVSKII, *Izvest. Akad. Nauk. SSSR Fiz. Ser.* **10** (1946) 477.
32. C. B. LUSHCHIK, *Soviet Phys. JETP* **3** (1956) 390.
33. V. MAXIA, S. ONNIS, and A. RUCCI, *J. Luminescence* **3** (1971) 378.

Received 7 February and accepted 27 March 1972.