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Analysis of the thermoluminescence from pure calcium sulphide single crystals, 8 to 300 K

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Thermoluminescence is measured from pure single crystals of calcium sulphide over the temperature range 8 to 300 K. The density of data gathered allows a range of analysis techniques to be applied. Four major peaks are found and analysis gives the thermal excitation energies as 0.25, 0.36 to 0.38, 0.73 and 0.68 eV for peaks near 108, 156, 228 and 261 K, respectively.

1. Introduction

The thermoluminescence (TL) of nominally pure single crystals of CaS from 8 to 300 K is presented and analysed. TL is obtained upon heating following excitation of the sample at a low initial temperature. Most workers employ a linear temperature rise rate (TRR) though other temperature profiles have been proposed [1, 2].

Significant difficulties arise in the interpretation of TL results. Most authors use as a starting point a basic single centre model of the trapping state. Regrettably, the first-order differential equations which describe this simple single centre model [3] do not admit an analytical solution.

A possible solution is to use a computer-hosted model to generate TL curves which may be compared with those obtained experimentally. This approach is considerably limited by the fact that there is a large number of parameters in the model with which one seeks to generate the TL curve, whilst the number of parameters accessible to direct experimental variation is very restricted (filling ratio, TRR, spectrum of emission and excitation). Most workers in the subject area would agree with the conclusion of Kelly *et al.* [4] that such a TL analysis of a single glow curve is ambiguous unless supported by some other experimental evidence. Saunders [5] suggested that one would have greater confidence in a proposed model if, with its chosen parameters fixed, it gave an accurate representation of a complete family of glow curves generated under different conditions of initial filling and TRR. This approach is developed in the present work.

2. The methods of analysis used on the TL

The first problem which is faced in analysing experimental TL data is that of obtaining a reasonable starting model and set of parameters. Over the years a considerable number of methods of analysis of TL curves has been proposed based upon a variety of assumptions relating to the properties inherent in the particular version of the single trap model considered [6, 7]. Much of this discussion was conducted in terms of the "order of the kinetics" involved and many expressions were deduced for obtaining the activation energy, E, for the particular conditions considered. Regrettably with an experimental TL peak it is often clear that even the single trap requirement is not met, much less the particular requirements for the application of one or other of the literature methods. Few, if any, of the methods include any self-checking facility which would expose the validity, or otherwise, of application in a given instance. Kivits and Hagebeuk [7], having reviewed the available literature methods, subjected a considerable number of them to the test of analysing computer-generated TL curves using a model of known parameters. Two major findings emerged:

(i) that the methods based upon using a variation of TRR to obtain E from the corresponding change in other parameters (e.g. temperatures of maximum emission, $T_{\max}$ and of half maximum emission T_1 and T_2, low and high temperature side, respectively, and intensity of emission, $I_{\max}$) are the most reliable and are largely independent of kinetic order (or retrapping ratio). Of these methods, that proposed by Hoogenstraaten [8] was found to be most reliable;

(ii) that there is considerable value in considering the predictions of a range of literature methods taken as a whole. By introducing known variations from the standard single centre model, the analysis of the resulting TL curves produced a characteristic profile of errors between the value of E produced by the different analysis methods. This raises the possibility of achieving the more difficult reverse process of deducing the variation from the profile using experimental TL results.

The essence of the method used is to hypothesize the variation from the standard model and to include this variation on the computer model to generate TL curves. The subsequent analysis of these curves should generate a similar profile to those found experimentally and the set of curves themselves should also

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TABLE I TL peaks for the two crystals. There is also a shoulder on the low temperature side of peak 3 at approx 207 K. Data were not collected above 230 K for crystal K at this TRR

	Peaks in crystal K				Peaks in crystal B			
	1	2	3	4	1	2	3	4
$T_{\max}$ (K)	105.0	147.5	221.4	–	105.8	155.6	222.7	258.2
TRR ($\mathrm{K\,sec^{-1}}$)	0.094	0.090	0.069	–	0.091	0.083	0.071	0.120

match closely. The advantage of the profile is that with experience in using it the type of variation responsible in a particular case readily suggests itself or, alternatively, certain possibilities are eliminated.

To enable a solution of the basic equations previously given [3] we developed a number of computer models. Whilst all our programs are capable of modelling the double trap represented by Equations 1 to 3 of [3], single trap behaviour may be modelled by setting $E_1 = E_2$. Both the exact and the approximate equations are modelled. The advantage of the latter is a reduced computation time once one has checked that one is modelling within a region where the approximations are valid [4].

The basis of the modelling was the Runge–Kutta–Merson fourth-order method [9]. The implementation involves setting initial values of concentrations of free electrons and trapped electrons at a chosen temperature and calculating their new values after an increment. The errors are also calculated and if these exceed a predetermined tolerance the step size is reduced.

3. Experimental procedure

A description of the experimental apparatus and of the structure, purity and excitation and fluorescence spectra of the crystals has been published [10]. For the present work, the important feature of the microcomputer-based experimental system is that considerable data are generated for each TL run (approx 10 000 data points). This enables high demands to be made when comparing experimental data with those generated by the model, provided that the experimental data themselves are reliable. This was ensured by close-fitting machining and positive keyed positioning on all the mechanical parts of the experimental apparatus. The result was that apparatus, including sample block, could be completely disassembled and reassembled with assurance that TL emission levels could be repeated within 1%, whilst corresponding temperatures were within 0.1 K.

4. Results

No TL emission was observed between 8 and 80 K following excitation at 5 K. Results from 77 K upwards were obtained for two crystals, identified as B and K. The TL emission was essentially the same for both, that for crystal B was previously published [10]. The similarity is evident from Table I.

To generate the family of curves to enable comparison of modelled and experimental TL curves, we varied the TRR and also the ratio of the initial traps which are filled. The latter was achieved by varying the time of excitation, with the filling ratio being obtained by evaluating the relative area under the resulting TL curve. The general behaviour is similar for each of the crystals; initially filling is proportional to excitation time, at higher filling there is a sublinear region and then saturation. Fig. 1 shows this for crystal K, the major difference from crystal B was that saturation was obtained after 50 sec rather than 600. Subsequently, each TL peak for each crystal was examined in detail for the manner in which its shape and intensity varied with filling ratio for a fixed TRR. The results for peak 2, crystal K, shown in Fig. 2 clearly suggest that this peak is not, after all, due to a single

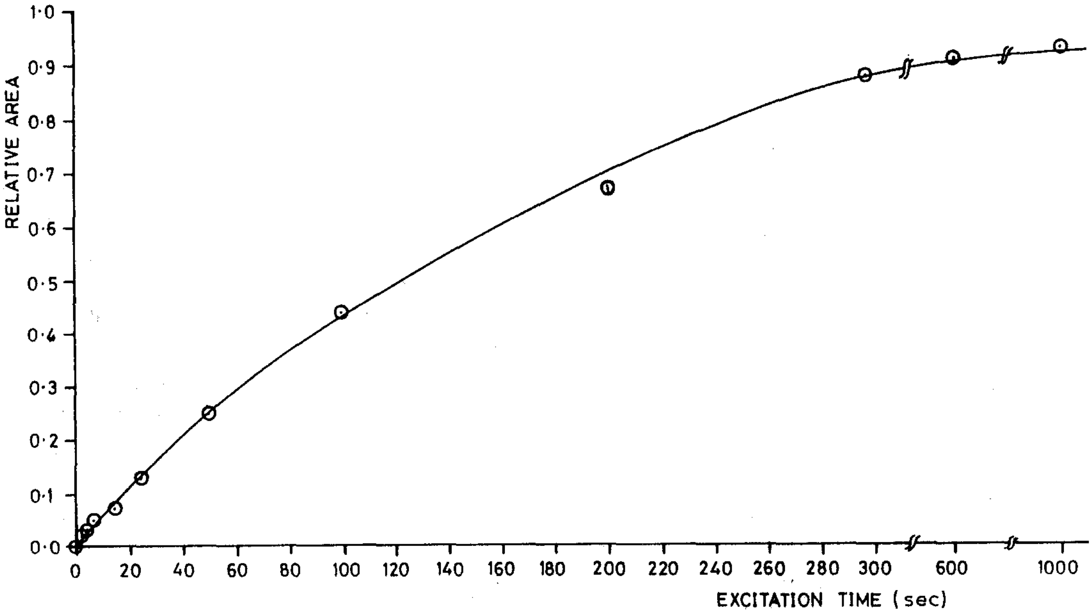

Figure 1 Area under peak 2 for crystal K as a function of excitation time.

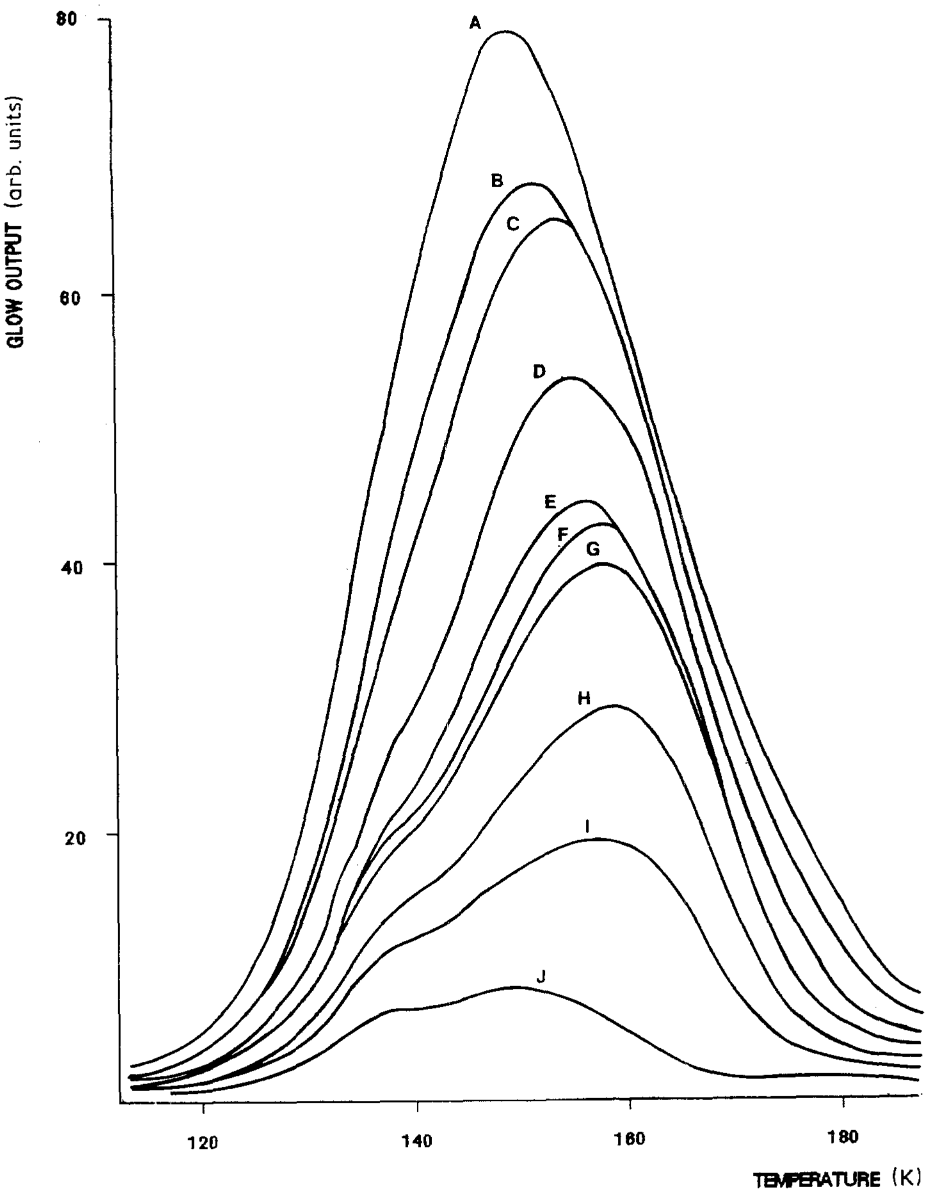

Figure 2 Experimental TL following different initial filling for peak 2, crystal K. TRR = 0.144 K sec^{-1}. For each curve approximately 10 000 data pairs of output and temperature were logged.

trapping state. The TL at the lower filling ratios indicates at least two traps present. Results for crystal B were very similar.

Results for different TRR for a fixed trap filling ratio were also obtained for each of the crystals. The results for crystal B are summarized in Table II. Occasional data are missing, because results were not taken over a sufficient range of temperatures, or adjacent peaks caused loss of this information. Hoogenstraaten plots [8] then permitted first estimates of trap parameters to be obtained for use on the computer model.

5. Analysis and discussion

Results from other literature methods, such as the initial rise [11] or the "area" method [12] may also be used to assist in the process of developing a starting model and parameters. The process whereby the profile produced from the model is matched to that produced experimentally, and the family of TL curves is also matched, is an iterative one. If the iteration allows a movement to a close match, the parameters of the model are considered as a useful representation of the trapping state(s). Perfect matches are never achieved, partly because of the stringency of the demands placed by the wealth of experimental data. Sometimes it is not possible to approach a close match at all and thus the inadequacy of the model is betrayed. In all cases a considerable number of iterative loops is worked through, the detail of each of these steps for each of the traps is not given in the following which summarizes the final conclusions.

5.1. Peak 1

This was identified as due to a single trap with first-order kinetics. The order was deduced from the peak shape and from the fact that the temperature of the maximum emission does not increase as the initial filling is reduced, see Table III.

A good fit to the curves generated by crystal K was obtained with the model $E = 0.246\,\text{eV}$, $S = 1.6 \times 10^{10}\,\text{Hz}$, $\delta = 10$, with 100 times as many deeper thermally disconnected traps. The model predictions are compared with experiment in Table IV. As always, the fit is not perfect. The model giving the best fit to the profile does not give the best TL curve fit; a higher δ, 50 gives a better fit in respect of Table IV and to the profile, but such a higher δ gives a small shift in maximum temperature at a trap filling ratio of 10% (not experimentally observed).

TABLE II Summary of results for varying TRR, crystal B

Peak	T_{max} (K)	I_{max} (arb. units)	TRR (K sec^{-1})	T_1 (K)	T_2 (K)
1	108.2	2489	0.296	100.9	113.1
3	228.4	23897	0.224	218.4	240.0
4	264.1	31673	0.222	247.8	–
1	105.8	1554	0.091	97.9	110.0
2	155.6	22175	0.083	137.4	168.2
3	222.7	12622	0.071	212.7	234.7
4	255.9	15936	0.067	240.6	–
1	107.3	2055	0.176	99.3	106.4
2	159.1	48960	0.150	143.1	171.2
3	225.1	21961	0.127	215.2	236.2
4	258.2	24101	0.120	242.6	276.4
1	109.4	3741	0.340	–	118.0
2	163.1	86972	0.285	144.5	176.1
3	229.0	39787	0.240	218.1	241.6
4	263.0	46444	0.237	245.6	284.5
1	104.0	873	0.051	98.7	104.9
2	155.4	23433	0.052	141.0	166.3
3	220.4	8654	0.048	210.1	231.1
4	252.1	10454	0.044	236.9	269.4
1	106.6	1838	0.125	99.5	112.1
2	159.2	44916	0.108	143.2	170.3
3	223.7	15060	0.091	213.3	–
4	255.7	19002	0.086	239.9	274.9
1	104.2	971	0.059	96.3	104.3
2	155.9	20143	0.054	140.9	166.4
3	220.0	6660	0.046	210.2	231.1
4	251.0	8382	0.041	236.4	267.8
1	108.2	3261	0.178	100.3	112.4
2	160.5	86398	0.151	144.1	173.6
3	225.9	38129	0.126	215.7	237.3
4	259.1	40855	0.123	242.8	–
1	108.3	3268	0.244	100.8	112.6
2	162.7	80294	0.206	144.9	174.8
3	227.6	29280	0.173	216.3	–
4	260.6	37405	0.168	243.5	282.0
1	105.3	1151	0.072	99.3	104.4
2	156.7	23463	0.063	141.2	167.0
3	220.8	7312	0.053	210.7	–
4	252.8	10186	0.050	238.1	270.7

5.2. Peak 2

In early attempts to model trap 2, the profile had been observed to be very close to that expected from a single trap with a high retrapping ratio, and good agreement between theory and experiment in terms of the profile generated and curve shape had been obtained using the single trap model $E = 0.463$ eV, $S = 3.2 \times 10^{12}$ Hz, $\delta = 200$. Support for this model was enhanced when it was used to predict the shift in T_{max} as the filling of traps was reduced, because the predictions were quite accurate down to 35% filling ratio (Table V). However, at small filling ratios, the prediction became inaccurate and two separate peaks became apparent in the experimental curves (Fig. 2).

It was also possible to obtain curves A to H of Fig. 2 using a two trap model. Indeed the curves could be matched a little more closely as might be expected, because extra parameters are available for adjustment. The best such model had parameters $E_1 = 0.35$ eV, $E_2 = 0.38$ eV, $\delta_1 = \delta_2 = 200$, $S_1 = S_2 = 3.2 \times 10^{12}$ Hz. However, experimentally, a reducing T_{max} was observed as the filling ratio is reduced below 0.35. To model this, it would appear that one need simply hypothesize that the shallower trap fills more quickly than the deeper one at lower excitation photon flux. However, for two traps connected only via the conduction band and with high retrapping ratios, as the initial population of the deeper trap is reduced most of the carriers emptied from the shallower trap are retrapped by the deeper one rather than recombine, so that the eventual TL is characteristic of the deeper trap. Thus, however different the filling rates, T_{max} always increases as filling is reduced. To explain curves I and J of Fig. 2 one has to postulate that each trap and recombination centre are isolated centres and no (or little) carrier traffic occurs via the conduction band. Before taking

TABLE III Experimental T_{max} variation, crystal B, as initial trap filling ratio is reduced. The ratio given is for peak 2. TRR = 0.29, 0.24, 0.20 and 0.20 K sec^{-1} for peaks 1 to 4, respectively

Trap filling ratio	T_{max} (K)			
	Peak 1	Peak 2	Peak 3	Peak 4
1.0	108.5	161.4	227.8	261.4
0.67	108.6	163.6	228.7	261.9
0.44	108.8	162.3	229.6	261.9
0.25	108.6	158.9	231.3	261.6
0.13	108.7	157.3	–	261.7
0.07	108.7	156.1	–	262.2

TABLE IV Comparison of model (peak 1) with experiment for selected TRR. Experimentally no shift in T_{max} is observed between traps full and 10% full

TRR (K sec^{-1})		T_{max} (K)	T_1 (K)	T_2 (K)
0.034	Experiment (E)	103.3	95.5	108.0
	Model traps full (TF)	101.5	96.5	105.1
	Model traps 10% full (T10F)	101.7	96.8	105.2
0.094	E	105.0	99.0	108.5
	TF	105.0	99.7	108.9
	T10F	105.2	100.0	109.1
0.149	E	106.6	100.0	110.8
	TF	106.6	101.1	110.7
	T10F	106.9	101.5	110.8
0.180	E	106.8	101.6	110.2
	TF	107.4	101.8	111.5
	T10F	107.6	102.1	111.6

TABLE V Comparison of experimental T_{max} variation with theory, peak 2. Experiment crystal K, TRR = 0.143 K sec^{-1}; theory, single trap model $E = 0.364$ eV, $S = 3.2 \times 10^{12}$ Hz, $\delta = 200$

Trap filling ratio	Experimental T_{max} (K)	Model T_{max} (K)
1.0	150	150.3
0.82	154	151.1
0.63	155	154.1
0.49	158	156.0
0.35	159	158.8
0.24	157	161.7
0.08	148	169.0

TABLE VI Application of the "area" method to peak 2

	Area (%)								
	10	20	30	40	50	60	70	80	90
Energy predicted (eV)	0.33	0.35	0.38	0.38	0.39	0.39	0.39	0.40	0.40

the analysis further along this line of reasoning we would require further experimental evidence, for example that no TSC is observed.

Further evidence that at least two traps were responsible for peak 2 was obtained when the "area" method of Sweet and Urquhart [12] was applied. This gave the results indicated in Table VI. Taken on their own these data would indicate two traps at (or a range of traps between) 0.35 and 0.40 eV. There is thus close agreement between this analysis and the conclusion from modelling.

5.3. Peaks 3 and 4

Peaks 3 and 4, whilst clearly due to at least two traps, do pose special problems for analysis. They overlap to such an extent that none of the methods in the literature based on individual peak geometry may be applied; correspondingly, the profile method is of limited use. Furthermore, even the initial rise method on peak 3 is denied to us as there is a small shoulder present on the low temperature side of this TL peak exhibited by both crystals. The "area" method is not available as data at the high-temperature side of peak 4 are incomplete so that the total area is unknown. Modelling using the two trap model is complicated, because at high enough temperatures to complete the curve for peak 4 the escape rate from peak 3 is such as to strain the computational method. At best this leads to long computing times, at worst to a breakdown. We are left with the varying TRR methods, applied at the emission peaks only.

It was possible to improve the situation slightly because it was established that the emission for peak 3 was predominantly at 506 nm whilst for peak 4 the emission wavelength was in excess of 587 nm. Thus by using interference filters, some enhancement of the individual peaks was possible. The parameters obtained are given below (Section 6). Evidence from Table III indicates that peak 4 is first order (no peak shift with filling ratio) whilst the slight shift to larger $T_{\max}$ indicates a probable second-order kinetics for peak 3.

Peaks 3 and 4 have been separately modelled on the basis of their experimental parameters together with the inherent limitations imposed by such limited experimental evidence. No contrary indications resulted.

6. Conclusions

The thermoluminescence peaks in the range 8 to 300 K for CaS have been subjected to analysis. The trap parameters obtained are given in Table VII.

References

1. A. HALPERIN, M. LEIBOWITZ and M. SCHESINGER, *Rev. Sci. Instrum.* **38** (1962) 1168.
2. W. ARNOLD and H. SHERWOOD, *J. Chem. Phys.* **62** (1952) 2.
3. M. A. S. SWEET and D. URQUHART, *Phys. Status Solidi* (*a*) **59** (1980) 223.
4. P. KELLY, M. J. LAUBITZ and P. BRAUNLICH, *Phys. Rev. B* **4** (1971) 1960.
5. I. J. SAUNDERS, *J. Phys. C.* **2** (1969) 2181.
6. S. W. S. McKEEVER, "Thermoluminescence of Solids" (Cambridge University Press, 1985).
7. P. KIVITS and H. J. L. HAGEBEUK, *J. Luminescence* **15** (1977) 1.
8. W. HOOGENSTRAATEN, *Philips Res Repts.* **13** (1958) 515.
9. J. D. LAMBERT, "Computational Methods in Ordinary Differential Equations" (Wiley, 1973) pp. 131–132.
10. M. A. S. SWEET *et al.*, *Phys. Status Solidi* (*a*) **84** (1984) K75.
11. G. F. J. GARLICK and A. F. GIBSON, *Proc. Phys. Soc.* **60** (1948) 574.
12. M. A. S. SWEET and D. URQUHART, *J. Phys. C* **14** (1981) 773.

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TABLE VII Trap parameters

Trap	E (eV)	S (Hz)	δ	Comment	Effective dynamics
1	0.246	1.6×10^{10}	10	100× deeper traps	First order
2	0.35/0.38	3.2×10^{12}	200	Double trap/trap band	High order
3	0.73 ± 0.06	5×10^{14}	1	Limited modelling	Second order
4	0.68 ± 0.06	2×10^{11}	0.1	Largely empirically based	First order

The parameters for trap 1 are presented with confidence. The description of trap 2 is incomplete in that the behaviour at low trap filling ratio is not completely explained unless isolated centres are hypothesized. Traps 3 and 4 have not been subjected to the same fullness of treatment as the others, and the confidence level is moderate only.