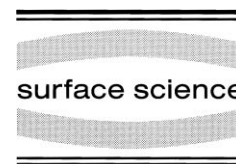




ELSEVIER

Surface Science 400 (1998) 258–265



Evaluation of parameters from thermal desorption spectra – methods borrowed from the analysis of thermoluminescence

R. Chen

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv 69978, Israel

Received 21 July 1997; accepted for publication 4 November 1997

Abstract

A number of methods for extracting the activation energy, pre-exponential factor and reaction order associated with the Polanyi–Wigner rate formulation have been reported in the literature. An entirely analogous equation had been utilized in the study of thermoluminescence (TL) and several methods have been developed for the extraction of the relevant parameters. Some of these methods are practically identical to those developed for the study of thermal desorption, whereas others have not been developed for thermal desorption but can be used with only very minor adjustment to the analysis of thermal desorption curves. In the present work, the utilization of the methods developed for the analysis of TL for the study of thermal desorption data is advocated. © 1998 Elsevier Science B.V.

Keywords: Computer simulations; Luminescence; Models of surface kinetics; Thermal desorption spectroscopy

1. Introduction

In the study of thermal desorption spectroscopy (TDS), also termed temperature programmed desorption (TPD), the Polanyi–Wigner equation is usually assumed to govern the process, namely [1–4],

$$r = -d\theta/dt = v(\theta)\theta^x[-E(\theta)/RT], \quad (1)$$

where r is the rate of desorption, θ is the adsorbance coverage, t is the time, T is the absolute temperature, v is the pre-exponential factor of desorption, x is the order of desorption, $E(\theta)$ is the activation energy of desorption and R is the gas constant. Whereas some researchers assumed only integer values of x (zero order, first order, etc.), others considered the possibility of non-

integer values of x [5]. In the particular first-order case, the pre-exponential factor v has dimensions of s^{-1} and is usually termed the “frequency-factor”. It is to be noted that although v and E are basically coverage dependent, these dependencies are often very weak and can be ignored [3,4,6]. Methods have been developed for the determination of the relevant parameters based on different features of the shape of the peak in question and its variation with the heating rate [3]. It should be noted that the activation energy is usually given in cal/mol, whereas the gas constant is $R = 1.9823$ cal/(mol K).

Thermoluminescence (TL) is a physical phenomenon in which a solid sample, typically an insulator, after absorbing energy while being irradiated at a given temperature by, say, nuclear radiation, X-rays etc., is being heated and emits light in the

shape of peaks of light emission intensity versus temperature. The basic theory of TL [7] has to do with imperfections in the crystal in question, impurities or defects. A single TL peak results from electronic transitions between a trapping state, the conduction band and a recombination center [7,8]. Basically, the process of these transitions leading to the occurrence of a TL peak are governed by a set of three simultaneous, nonlinear differential equations in the concentrations of carriers in trapping states, the conduction band and the recombination center. Making some simplifying approximations, including the “quasi-equilibrium” assumption, different investigators [9,10] reached a single differential equation governing the process, namely:

$$I(t) = -dn/dt = s'n^b \exp(-E/kT), \quad (2)$$

with $b=1, 2$. Here, n is the concentration of trapped carriers, b is the kinetics order, s' is the pre-exponential factor, which in the case of $b=1$ (first-order kinetics) is usually denoted by s and has dimensions of s^{-1} ; E is the activation energy, usually given in electronvolts and k is the Boltzmann constant.

It should be noted here that once a certain heating function $T=T(t)$ is chosen in the experiment, $I(t)$ on the left hand side of Eq. (2) can be replaced by $I(T)$. It is customary to choose the linear heating function $T=T_0+\beta t$, where β is the heating rate. The hyperbolic heating function $T=T_0/(1-\beta't)$, where β' is a constant with s^{-1} units, has some theoretical advantage, but is harder to attain experimentally. In fact, for some purposes, any heating function $T(t)$ can be utilized, providing it is monotonically increasing. The instantaneous heating rate in this general case is, obviously defined by $\beta=dT/dt$.

It is evident that there is a direct analogy between Eqs. (1) and (2), with two minor differences. Eq. (1) is in θ which is a relative coverage defined in Ref. [4] as N_{ad}/N_s , where N_{ad} is the adsorbed concentration of particles and N_s the concentration of active sites on the surface; n in Eq. (2) is the concentration of carriers per unit volume. Eq. (2) can easily be made very similar to Eq. (1) by dividing both sides of the equation by the total concentration of traps of the relevant

kind N and defining $\theta=n/N$. In addition, although E and R in Eq. (1), on the one hand, and E and k in Eq. (2) do not have the same dimensions, E/R in the former and E/k in the latter are exactly the same since the gas constant R is just the product of the Boltzmann constant k and the Avogadro number. This completes the analogy between the two equations. A final point to be mentioned in this respect is that orders of kinetics b other than 1 or 2 have been considered for TL, either in a specific case in which $b=1.5$ [11], which appears to result from the special physical conditions, or as a very useful empirical approach [12] yielding different shapes of the TL peak which are found for various experimental peaks. In parallel, thermal desorption with fractional order has also been discussed in the literature [13].

2. TL methods for parameter evaluation

In this section, a comparison is made between similar methods for evaluating kinetic parameters in TL and in thermal desorption. Special attention will be given to methods developed in the study of TL which have some specific advantage and no parallel developed for thermal desorption curves. Thus, they can be utilized, practically unaltered, by researchers investigating thermal desorption. The presentation here will use the TL terminology, namely looking at the Arrhenius function as $\exp(-E/kT)$ with E in electronvolts and k Boltzmann's constant. As explained above, the translation into the thermal desorption language is immediate.

As pointed out by Garlick and Gibson [10] as early as 1948, irrespective of the details of the TL kinetics, as long as one concentrates on the “initial-rise” range, one can write:

$$I(T) \propto \exp(-E/kT). \quad (3)$$

Thus, a plot of $\ln[I(T)]$ versus $1/T$ is expected to yield a straight line with a slope of $-E/k$, from which the activation energy is readily evaluated. It has been pointed out that going up to $\sim 5\%$ of the maximum intensity would yield a good result for the energy and going up to $\sim 10\%$ of the maximum intensity may result in an error of 2–3% in the

evaluated value of E . The obvious disadvantage of this simple method is that it can be used yielding good results only for relatively high-intensity peaks. Practically the same method has been developed by Habenschaden and Küppers [14] for the study of thermal desorption and termed the “leading-edge analysis”.

The process of extracting the activation energy from the initial-rise range can be presented in a slightly different manner, namely calculating in the relevant range:

$$E_{\text{IR}} = -k \, d \ln I / [d(I/T)]. \quad (4)$$

It has been noted that the pre-exponential factor itself can be somewhat temperature dependent. In TL, dependencies like $s \propto t^a$ with $2 \geq a \geq -2$ have been considered [15,16]. Using the same procedure as above would yield a nearly straight line with a slope which, according to Eq. (4) is

$$E_{\text{IR}} = E + akT, \quad (5)$$

from which one can get the corrected initial-rise value

$$E = E_{\text{IR}} - akT. \quad (6)$$

The correction term $-akT$ is relatively small and therefore, being temperature dependent, it is irrelevant in the narrow temperature range utilized in the initial-rise method. Note that a similar power of temperature dependence of the pre-exponential factor has been considered in the study of thermal desorption curves (see, for example, Kreuzer and Payne [17]).

Another improvement of the initial-rise method was suggested by Halperin et al. [18]. In cases where the kinetics order b is known, it is suggested to plot $\ln(I/n^b)$ versus I/T . The straight line would now extend ideally to the whole temperature range of the peak. The value of n can be found from the interval over the peak from each specific point to the end of the peak. This may be complicated if more peaks at higher temperatures exist; in particular, the situation is difficult if there is a strong overlap between peaks. As for the order of kinetics b , if it is not known, one can try the plots with different values of b and find the best straight line. This is expected to yield the best value for the

activation energy as well as an estimate of the kinetics order. A very similar method for thermal desorption curves has been developed by Niemantsverdriet et al. [19].

3. Peak shape methods

Although the shape of the peak in TL as well as in thermal desorption depends on all the parameters, E , s' and b in Eq. (2), it has been shown that the shape of the normalized peak depends very strongly on the kinetic order b and very little on E and s' (or s in the first-order case). For $b=1$, the first-order solution of Eq. (2) is, for a linear heating function,

$$I(T) = n_0 \exp(-E/kT) \times \exp \left[-(s/\beta) \int_{T_0}^T \exp(-E/k\tau) \, d\tau \right]. \quad (7)$$

A synthetic, normalized computer calculated example of this expression is given in curve I of Fig. 1. The parameters used are given in the caption. For the evaluation of the integral, use has

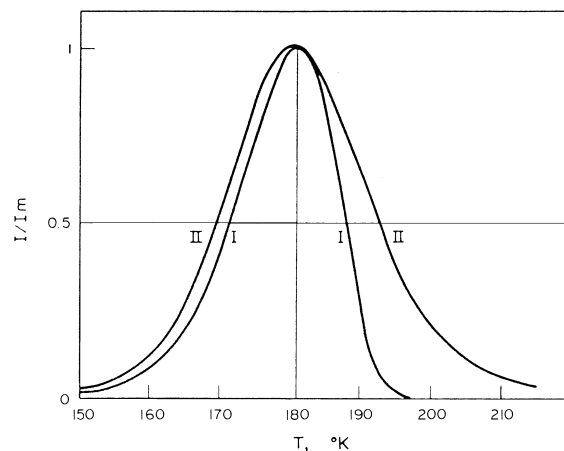


Fig. 1. A typical first-order peak calculated by the Randall-Wilkins equation (curve I) and a second-order peak (curve II). Both curves have been simulated numerically with $E=0.4$ eV. In curve I, the frequency factor is $s=10^{10} \text{ s}^{-1}$. In curve II, the pre-exponential factor is $s'=10^{-11} \text{ m}^3 \text{ s}^{-1}$.

been made of the asymptotic series

$$\int_0^T \exp(-E/k\tau) \cong T \exp(-E/kT) \times \sum_{n=1} (kT/E)^n (-1)^{n-1} n! \tag{8}$$

Some terms in this expansion have been utilized by researchers in both TL [7] and thermal desorption [1]. It has been shown by Chen [20] that the best accuracy using this series is attained by going to the term smallest in absolute value and adding one half of the next term.

The main feature of curve I is its being asymmetric, with the fall-off half being significantly narrower than the low-temperature half. This property has been given a quantitative measure by Halperin and Braner [7] who termed the maximum temperature by T_m and the low-and high temperatures by T_1 and T_2 . They then defined the full half-width $\omega = T_2 - T_1$, the low-temperature half-width $\tau = T_m - T_1$ and the high-temperature half-width $\delta = T_2 - T_m$. By the use of these magnitudes, the shape factor

$$\mu_g = \delta/\omega, \tag{9}$$

has been defined. It has been shown [6] that first-order peaks are characterized by $-\mu_g \approx 0.42$, with rather slight dependence on the other two parameters E and s . The solution of Eq. (2) for $b=2$ and linear heating function is

$$I(T) = n_0^2 s' \exp(-E/kT) \times \left[1 + (n_0 s' / \beta) \int_{T_0}^T \exp(-E/k\tau) d\tau \right]^{-2} \tag{10}$$

A typical curve of this form is II in Fig. 1, calculated for the parameters given in the caption. A typical value of the shape factor in this case is $\mu_g \approx 0.52$, again with slight variation with different E and s' values. These values of μ_g mean that second-order peaks are nearly symmetrical. Halperin and Braner [7] have developed methods for evaluating the activation energy by using the shape of the peak. These have been modified by Chen [16] who gave simple formulas for evaluating E , based on the measurement of T_m as well as

either τ , δ or ω . For example, for first-order peaks, the equation is

$$E_{\omega 1} = 2.52kT_m^2/\omega - (1 + 0.5a)2kT_m, \tag{11}$$

where a is the power in the dependence of the frequency factor on temperature, $s \propto T^a$; in many cases, a is assumed to be zero and the second term obviously becomes $-2kT_m$. For second-order kinetics, the formula is

$$E_{\omega 2} = 3.54kT_m^2/\omega + (1 + 0.5a)2kT_m. \tag{12}$$

It is to be noted that although the half-width equation appears very simple to use, widths at other fractions of the maximum intensity have later been used. These include 2/3 and 4/5 employed by Mazumdar et al. [21] in the study of TL as well as 3/4 utilized by de Jong and Niemantsverdriet [3] in the analysis of desorption curves.

For the general-order kinetics given in Eq. (2), the solution yields [13]

$$I(T) = s'n_0^b \exp(-E/kT) \left\{ [(b-1)s'n_0^{b-1}/\beta] \times \int_{T_0}^T \exp(-E/k\tau) d\tau + 1 \right\}^{-b/(b-1)} \tag{13}$$

Obviously, for $b=2$ one obtains Eq. (10). For $b=1$, the expression is meaningless, but it can be shown that as $b \rightarrow 1$, Eq. (13) goes to Eq. (7). It has been shown [13] that while changing b gradually from 1 to 2, the shape factor μ_g changes continuously from 0.42 to 0.52 (see Fig. 2). Chen [13] suggested using the measured value of μ_g as an interpolation factor which enables the evaluation of the activation energy for a broad range of the order parameter b .

An equation of the same family as Eqs. (11) and (12) for this general situation has been given [12] as

$$E_\omega = [2.52 + 10.2(\mu_g - 0.42)]kT_m^2/\omega - (1 + 0.5a)2kT_m, \tag{14}$$

where a is the power of temperature dependence of the frequency factor mentioned above and similar equations based on the low-temperature half-width τ and the high-temperature half width δ .

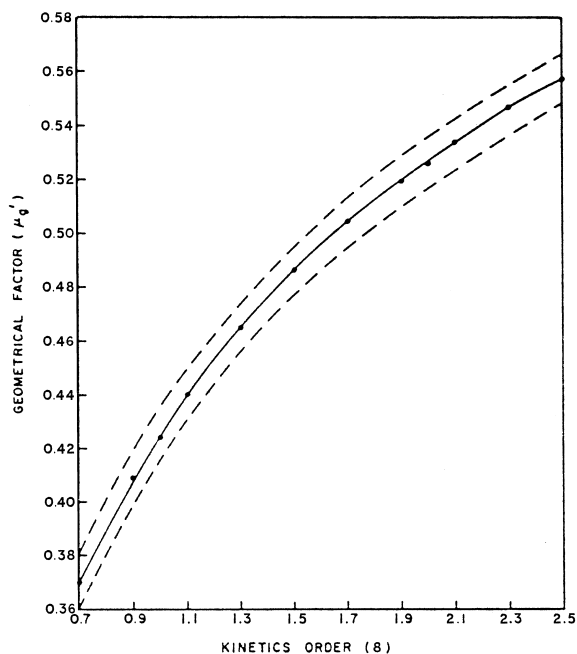


Fig. 2. Calculated shape factor μ_g as a function of the given order b . The central curve shows the average values; the upper and lower dashed lines give the largest and smallest values for different values of E and s' for each given order b .

The validity of these equations has been tested for synthetic, computer generated general-order peaks and yielded very good accuracy. Of course, exactly the same expressions can be used for the evaluation of the activation energy from thermal desorption peaks. It is to be noted that a different parameter has been defined for quantifying the skewness of the thermal desorption peak [3] based on the same measured magnitudes:

$$\chi = 100 \times (\delta - \tau) / \omega. \quad (15)$$

Although the scale here is entirely different than in the above-mentioned μ_g , basically it determines the same property using the same measured quantities. Also should be mentioned a work by Kelly and Laubitz [22] which showed that if a hyperbolic heating rate is utilized, namely, $T = T_0 / (1 - \beta' t)$ where β' is a constant with dimensions of s^{-1} simpler equations for the evaluation of the activation energy for first-order kinetics can be written as

$$E = 1.46kT_m T_1 / \tau = 0.985kT_m T_2 / \delta. \quad (16)$$

The difference of the numerical coefficient in these two expressions indicates the relatively large asymmetry of the first-order peak. As for second-order peaks, the analogous equations are

$$E = 1.763kT_1 T_m / \tau = 1.763kT_m T_2 / \delta \quad (17)$$

which yields $T_1 / \tau = T_2 / \delta$ from which one can immediately obtain

$$T_m^{-1} = 0.5(T_1^{-1} + T_2^{-1}). \quad (18)$$

This means that the peak is exactly symmetrical under these circumstances in reciprocal temperature, which also implies that it is nearly symmetrical in temperature as well. It should be noted that the advantage of using hyperbolic heating functions had been originally mentioned by Arnold and Sherwood [23] for TL peaks and by Ehrlich [24] for thermal desorption peaks.

4. Various heating rates

Let us consider again the Eq. (7) for a first-order curve with a linear heating function. As pointed out by Randall and Wilkins [9], the condition for the maximum, attained by equating the derivative of Eq. (7) to zero is

$$\beta E / (kT_m^2) = s \exp(-E/kT_m). \quad (19)$$

It is obvious that for a peak with given E and s , changing the heating rate β should change the maximum temperature T_m . Writing Eq. (19) as

$$\beta = (sk/E)T_m^2 \exp(-E/kT_m), \quad (20)$$

shows that when β increases, T_m should increase as well since the right-hand side of Eq. (20) is an increasing function of T_m . Booth [25], Bohun [26] and Parfianovitch [27] showed independently that if one utilizes two linear heating rates β_1 and β_2 and gets two maxima T_{m1} and T_{m2} , the use of Eq. (19) twice yields an explicit expression for the activation energy:

$$E = [kT_{m1} T_{m2} / (T_{m1} - T_{m2})] \ln[(\beta_1 / \beta_2) (T_{m2} / T_{m1})^2]. \quad (21)$$

This value can be re-inserted into Eq. (19) to yield the value of the frequency factor s . Hoogenstraaten

[28] suggested the use of several (constant) heating rates; having performed this, a plot of $\ln(T_m^2/\beta)$ versus $(1/T_m)$ should yield a straight line from the slope of which, E/k , E can readily be found. Extrapolation to $1/T_m=0$ gives the value of $\ln(sk/E)$ from which s can be calculated by the insertion of E/k found from the slope.

Osada [29] extended the method for nonlinear heating functions. He proved that Eq. (19) is valid for an exponential heating function $T = T_\infty - (T_\infty - T_0) \cdot \exp(-\alpha t)$ where α is a constant (s^{-1}) and T_∞ the final temperature approached asymptotically with time. This heating scheme is the one we obtain “naturally” if we let a cold sample warm up, while being in thermal contact with an infinite thermal bath at temperature T_∞ . The *instantaneous* heating rate at T_∞ which we can denote by β_m should now replace β in Eqs. (19) and (20). This leads directly to the validity of Eq. (21) for various exponential heating functions as well as to the use of the Hoogenstraaten method in this case. A remark to the same effect, related to thermal desorption curves, can be found in a recent work by García et al. [4]. Chen and Winer [30] have shown that, in fact, Eqs. (19) and (20) are correct for any first-order peak measured under any monotonically increasing heating function. This was performed by re-writing Eq. (7) as

$$I = n_0 s \exp(-E/kT) \times \exp \left[-s \int_T^T (d\tau/dt)^{-1} \exp(-E/k\tau) d\tau \right], \quad (22)$$

where $T(t)$ [or $\tau(t)$] is any heating function. The requirement that the heating function is monotonically increasing is in order to assure that $d\tau/dt \neq 0$. Setting the derivative of Eq. (22) to zero yields

$$\beta_m E/(kT_m^2) = s \exp(-E/kT_m), \quad (23)$$

where $\beta_m = (dT/dt)_m$. Obviously, the extension of Eq. (21) as well as the plot of $\ln(\mu_m/T_m^2)$ versus $1/T_m$ for the evaluation of the activation energy E can be readily performed in this general case. It can rather easily be shown that the method of plotting $\ln[I(T_m)]$ versus $1/T_m$ which had been

shown to yield a straight line with a slope of $-E/k$ with different constant heating rates can, in fact, be used with different nonlinear heating functions as well. This, of course, is true both for TL peaks [30] and for thermal desorption curves. It is clear that the hyperbolic heating function mentioned in the previous section, being a monotonically increasing function, is included in this general discussion.

Although rigorously proven only for first-order peaks, Chen and Winer [30] showed that the method can be utilized for non-first-order kinetics very successfully. They showed this for both computer generated second- and general-order peaks, as well as experimental TL peaks in $ZnS:Er^{3+}$, known not to be of first order. Further discussion on this point can be found in Ref. [15]. It should be noted that different investigators used the different heating-rate methods for TL peaks without checking the order of kinetics and with good results as far as the values of the parameters could be compared with results attained by other methods. A recent analogous discussion on thermal desorption curves of first- and second-order kinetics (though with linear heating functions only) has been given by Zhou et al. [31].

5. Curve fitting and deconvolution

The initial-rise (leading-edge) method mentioned above is concentrating on the shape of the peak at its low-temperature range. A method which appears to be more reliable is the curve fitting, using information from a broader range of the peak. Basically, this consists of simulating a TL or thermal desorption peak using a set of parameters, comparing it to the experimental curve in hand and varying the parameters used so as to get the best fit between the experimental and computed curves. In principle, this is very close to the formula given by García et al. [4] for thermal desorption peaks. Previous methods, developed for other thermally stimulated processes, can be considered instead. These include the works by Doyle [32] and Zsakó [33] used in the study of thermogravimetry, Cowell and Woods [34] in thermally stimulated conductivity and Mohan and Chen [35]

and Shenker and Chen [36] in the study of thermoluminescence.

García et al. [4] point out that more complex situations such as multiple peak spectrum should also be studied. The analogous situation of multiple peak TL curves with significant overlapping, which should be deconvoluted so as to yield all the relevant parameters, has been dealt with. A rather recent extensive review article by Horowitz and Yossian [37] sums up in detail the existing literature on this subject.

6. Conclusion

In the present work, the applicability of methods developed for the study of thermoluminescence (TL) curves as well as other thermally stimulated peaks for the analysis of thermal desorption curves is advocated. The close analogy between these basically different phenomena is discussed. This should encourage investigators in any of the above-mentioned fields to consider the analytical methods developed for the study of the other fields in this extended family to their own use. The group of methods mentioned include the initial-rise (leading-edge) method and its extensions, peak shape methods, various heating rate methods and curve fitting along with deconvolution methods. Another group, namely the isothermal decay methods has also been developed in parallel by researchers of luminescence and thermal desorption; details have not been given since this is not a genuine thermal curve, but rather, the dependence of the measured property is on time at a constant temperature.

Finally, the possibility of continuous distributions of energy states and pre-exponential factors associated with thermal desorption spectra have been discussed by Seebauer [38]. It should be noted that these possibilities have been considered concerning the thermally stimulated process of ionic thermal conductivity (ITC) [39] as well as in TL. Different continuous distributions of activation energies such as the Gaussian [40] have been suggested. In addition, the possibility of a continuous distribution of the frequency factor in TL has been considered [41].

References

- [1] P.A. Redhead, *Vacuum* 12 (1962) 203.
- [2] D.A. King, *Surf. Sci.* 47 (1975) 384.
- [3] A.M. de Jong, J.W. Niemantsverdriet, *Surf. Sci.* 233 (1990) 355.
- [4] V.J. García, J.M. Briceño-Valero, L. Martinez, *Surf. Sci.* 339 (1995) 189.
- [5] M. Smutek, *Vacuum* 24 (1974) 173.
- [6] E. Bornand, *Surf. Sci.* 152153 (1985) 314.
- [7] A. Halperin, A.A. Braner, *Phys. Rev.* 117 (1960) 408.
- [8] R. Chen, S.W.S. McKeever, *Theory of Thermoluminescence and Related Phenomena*, World Scientific, Singapore, 1997.
- [9] J.T. Randall, M.H.F. Wilkins, *Proc. Roy. Soc. Lond. A* 84 (1945) 366.
- [10] G.F.J. Garlick, A.F. Gibson, *Proc. Phys. Soc.* 60 (1948) 574.
- [11] C.E. May, J.A. Partridge, *J. Chem. Phys.* 40 (1964) 1401.
- [12] R. Chen, *J. Electrochem. Soc.* 116 (1969) 1254.
- [13] M. Vollmer, F. Träger, *Surf. Sci.* 187 (1987) 445.
- [14] E. Habenschaden, J. Küppers, *Surf. Sci.* 138 (1984) L147.
- [15] R. Chen, Y. Kirsh, *Analysis of Thermally Stimulated Processes*, Pergamon Press, Oxford, 1981.
- [16] R. Chen, *J. Appl. Phys.* 40 (1969) 570.
- [17] H.J. Kreuzer, S.H. Payne, in: C.T. Rettner, M.N.R. Ashfold (Eds.), *Dynamics of Gas-Surface Interactions*, The Royal Society of Chemistry, Cambridge, 1991.
- [18] A. Halperin, A.A. Braner, A. Ben-Zvi, N. Kristianpoller, *Phys. Rev.* 117 (1960) 416.
- [19] J.W. Niemantsverdriet, P. Dolle, K. Markert, K. Wandelt, *J. Vac. Sci. Technol. A* 5 (1987) 875.
- [20] R. Chen, *J. Comput. Phys.* 8 (1971) 156.
- [21] P.S. Mazumdar, S.J. Singh, R.K. Gartia, *J. Phys D: Appl. Phys.* 21 (1988) 815.
- [22] P.J. Kelly, M.J. Laubitz, *Can. J. Phys.* 45 (1967) 311.
- [23] W. Arnold, H. Sherwood, *J. Phys. Chem.* 63 (1959) 2.
- [24] G. Ehrlich, *J. Appl. Phys.* 32 (1961) 4.
- [25] A.H. Booth, *Can. J. Chem.* 32 (1961) 4.
- [26] A. Bohun, *Czech. J. Phys.* 4 (1954) 214.
- [27] I.A. Parfianovitch, *J. Exp. Theor. Phys. SSSR* 26 (1954) 696.
- [28] W. Hoogenstraaten, *Philips Res. Repts* 13 (1958) 515.
- [29] K. Osada, *J. Phys. Soc. Jap.* 15 (1960) 145.
- [30] R. Chen, S.A.A. Winer, *J. Appl. Phys.* 41 (1970) 5227.
- [31] S. Zhou, G. Schulz-Ekloff, D. Popovic, *J. Therm. Anal.* 41 (1994) 767.
- [32] C.D. Doyle, in: P.E. Slade, L.T. Jenkins (Eds.), *Techniques and Methods for Polymer Evaluation*, Dekker, New York, 1966.
- [33] J. Zsakó, *J. Phys. Chem.* 72 (1968) 2406.
- [34] T.A.T. Cowell, J. Woods, *Brit. J. Appl. Phys.* 18 (1967) 1045.
- [35] N.S. Mohan, R. Chen, *J. Phys. D: Appl. Phys.* 3 (1970) 243.

- [36] D. Shenker, R. Chen, *J. Comput. Phys.* 10 (1972) 272.
- [37] Y.S. Horowitz, D. Yossian, *Radiat. Prot. Dosim.* 60 (1995) 1–113.
- [38] E.G. Seebauer, *Surf. Sci.* 316 (1994) 391.
- [39] E. Laredo, A. Bello, N. Suarez, M. Diaz, *Phys. Stat. Sol. (a)* 121 (1991) K121.
- [40] W.F. Hornyak, A.D. Franklin, R. Chen, *Ancient TL* 11 (1993) 21.
- [41] C. Christodoulides, *Phys. Stat. Sol. (a)* 118 (1990) 333.