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# Resolving overlapping peaks in differential scanning calorimetry

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In this work, a Gaussian function is fitted to exothermal peaks obtained through differential scanning calorimetry of amorphous semiconducting alloys. The validity of the approximation is tested by calculating the parameters $E$ (activation energy), $K_0$ (frequency factor) and $n$ (reaction order) which define the crystallization kinetics of two different alloys belonging to the Ge–As–Te and Cu–As–Te systems. Finally, the approximation is used to resolve thermographic peaks, by a numerical method, being applied to the kinetic study of two alloys in the Cu–As–Te glassy system which exhibit multiple peaks.

## 1. Introduction

The experimental determination of physical magnitudes through analogical methods often leads to graphic registers whose shape (fig. 1(a)) allows them to be given the generic name of *peaks*. An analysis of the variables represented in the ordinates in relation to the values corresponding to the abscissas, based on a certain theoretical formalism, makes it possible finally to gain a knowledge of the mechanism governing the measured phenomenon. However, it often happens that because the phenomenon is complex or difficult to isolate or because the measurement technique itself causes intrinsic interactions, the experimental registers obtained are two or more overlapping peaks, as seen in fig. 1(b) or (c). In these cases, the theoretical conclusions reached for a single process are not applicable, since there is an abscissa interval in which no experimental data are available for the magnitude represented in the ordinate, concerning a single phenomenon, but for the added values of the same for two simultaneous processes.

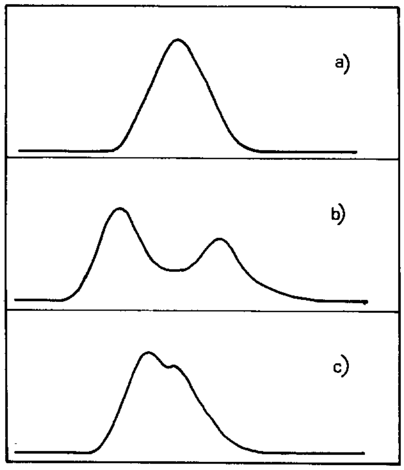

Fig. 1. Examples for exothermal DSC peaks.

The problem is generically called *overlapping*, and to discern the contribution of each one of the phenomena to the value of the ordinate, in the common abscissa interval, is to resolve both peaks. The problem of resolving the peaks obviously presents various degrees of difficulty, in relation to the degree of overlapping. The overlapping can vary between a minimum overlapping, in which the second process begins where the first is finishing, or a high degree of overlapping, in which both phenomena are nearly simultaneous. In the former case, the existence of the overlapping may even be ignored; in the latter, the resolution might be so uncertain as to assume a single process.

Although the problem has been presented generically, being common to a great variety of physical problems, in this work it will be limited to differential scanning calorimetry (DCS) experimental techniques, carried out by continuous heating, and applied to the study of the crystallization kinetics of bulk amorphous materials.

This DSC technique gives curves whose abscissas correspond to temperatures (times), and whose ordinates register the instantaneous power that the oven gives the sample, in order to maintain the programmed thermal growth. When the crystallization process begins, implying an exothermic reation, the power required varies, depending on the amount of glassy material that is gradually added to the crystallization reaction; thus, a typical exothermal peak is registered which goes from the start of the reaction to the crystallization of the whole sample. Certain glassy alloys exhibit several stages of crystallization, affecting more elementary compounds chemically produced during the reaction, or compounds with the same elements as the original, but with different stoichiometries. Therefore, the data obtained exhibit all the casuistry mentioned in the overlapping of crystallization peaks.

In order to solve the problem of two overlapping peaks, the first thing one must know is the general shape of the curve corresponding to a single crystallization process. Then a mathematical approximation to it is deduced, so that by applying the same analysis to this approximation as to the experimental one, equal kinetic parameters are obtained, or with differences below the working error. Based on the assumed theoretical function, it will then be possible to discern the two basic reactions from which the overlapping DSC data originate.

## 2. Theoretical function associated to a single crystallization peak

The theory of the crystallization processes is well represented by the formalism of Johnson–Mehl–Avrami [1–3] which, through different analytical procedures, and from the experimental data, makes it possible to obtain the three parameters which define the crystallization reaction: $E$ (activation energy), $n$ (reaction order) and $K_0$ (reaction frequency factor).

It is more convenient, for our present purposes, to represent the exothermic peaks as crystallization fraction rates $x$, as the ordinate, versus time (temperature), as the abscissa. This relation is given by the relation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{A}\left[\frac{\mathrm{d}Q}{\mathrm{d}t}\right] \tag{1}$$

existing between the power supplied $\mathrm{d}Q/\mathrm{d}t$ (mcal/s), the crystallization rates $\mathrm{d}x/\mathrm{d}t$ ($\mathrm{s}^{-1}$), and the total area $A$ (mcal) enclosed by the peak. The analyzed peaks are therefore seen as belonging to the family of *frequency curves* (normalized to unity).

It is not our present purpose to find a mathematical function, or superposition of functions which describe the experimental peak with complete rigour. A compromise between mathematical simplicity and the greatest degree of approximation between the kinetic parameters derived from the theoretical curve and those obtained from the experimental peak is sought.

The theoretical function which has given the best results belongs to the family of Gaussian functions:

$$\mathrm{f}(t) = a\ \mathrm{e}^{-b(t-t_0)^2} \tag{2}$$

where $a$ and $b$ are adjusted to each individual experimental peak in such a way that

$$S = \sum_{i=1}^{N}\left(y_i - a\ \mathrm{e}^{-b(t_i-t_0)^2}\right)^2 \tag{3}$$

is minimal, $y_i$ being the ordinates corresponding to the $N$ abscissas, $t_i$, of the experimental peak. The constant $t_0$ is the value of the abscissa (temperature or time) at which the crystallization rate is a maximum. It is a simple translation factor for making the maximum values of the experimental and theoretical curves coincide. The function described by eq. (2) is denoted from now on as associated theoretical function (ATF).

The adoption of these ATFs to fit the exothermal peaks given by the DSC admits an immediate formal objection: ATFs are symmetrical, with respect to the value of the ordinate at which

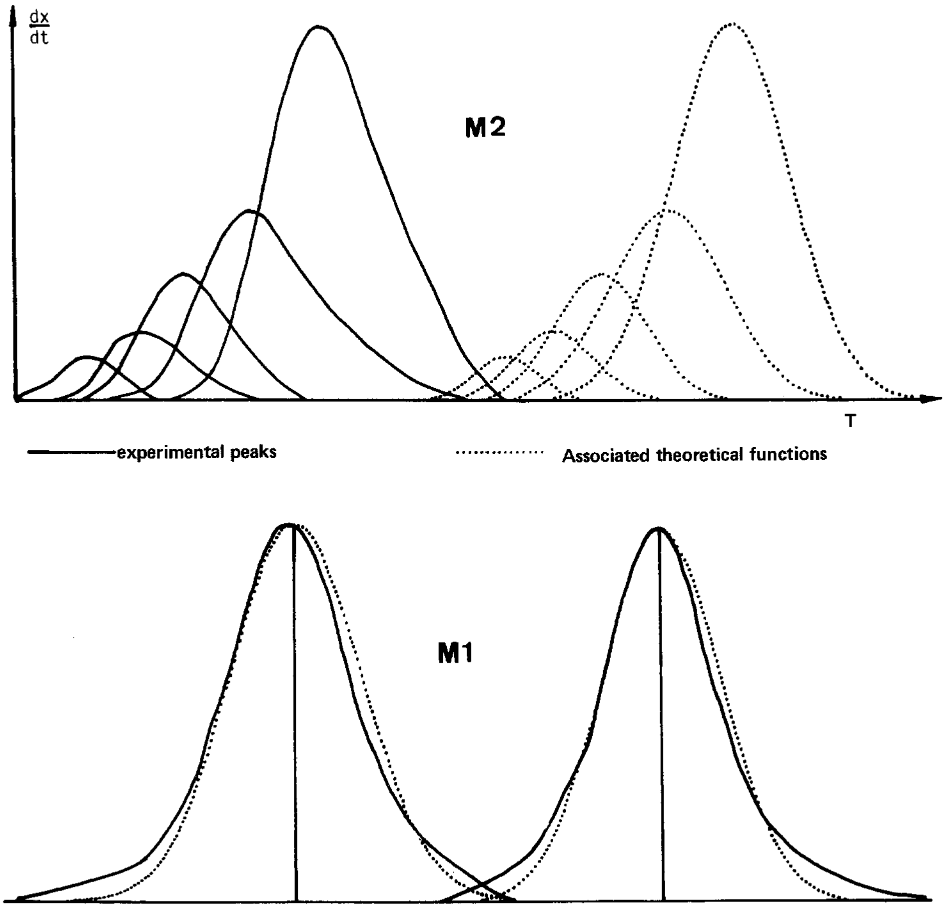

Fig. 2. Experimental curves and associated theoretical functions for different alloys. M1 = $Ge_{0.14}As_{0.43}Te_{0.43}$; M2 = $Cu_{0.10}As_{0.40}Se_{0.50}$.

the maximum is observed. Experimental peaks do not exhibit this symmetry, as shown in the adjustment represented in fig. 2, and as deduced from the theoretical Johnson–Mehl–Avrami model. This model points out that the maximum crystallization rate is reached when the crystallization fraction is $x = 0.63$ [4,5]. A correction for this difference could be introduced by an appropriate asymmetry factor in eq. (2). However, the good agreement existing between the areas limited by the experimental peaks and the ATFs, as well as between the kinetic parameters deduced from both curves, have made it advisable to use the above mentioned ATFs, with no corrections, for the sake of formal simplicity.

The minimization of expression (3) can be formally solved by imposing the conditions

$$\delta S/\delta a = 0, \quad \delta S/\delta b = 0. \qquad (4)$$

However, this minimization does not guarantee that the maximum ordinate of the ATF will coincide exactly with the maximum experimental value. This fact is very important, since some techniques for calculating kinetic parameters rely on experimental data obtained from different heating rates [5–7]. In order not to lose this condition and, at the same time, to minimize $S$, we have opted for making the value of parameter a coincide with the maximum experimental ordinate. Carrying out the minimization with $\delta S/\delta b = 0$, with the result that, in order for S to be minimal, it must be true that

$$\sum_{i=1}^{N}[t_i-t_0]^2 y_i\, \mathrm{e}^{-(t_i-t_0)^2} = a\sum_{i=1}^{N}[t_i-t_0]^2\, \mathrm{e}^{-2b(t_i-t_0)^2}, \qquad (5)$$

a condition that can be easily imposed on the experimental data by a numerical procedure, giving the needed value of parameter $b$. In this way, the exothermic peak registered by the DSC for a single crystallization process can be approximated by an ATF deduced from the experimental data of the peak itself.

In order to verify the validity of the method, glassy alloys, $Ge_{0.14}As_{0.43}Te_{0.43}$ (M1) and $Cu_{0.10}As_{0.40}Se_{0.50}$ (M2), were chosen, their crystallization kinetics having been previously studied [4,6], and the corresponding ATFs were adjusted. Figure 2 shows the graphic representation of these, and the experimental curves for M2, as well as the superposition of both, for two heating rates, in the case of sample M1.

In order to study the crystallization kinetics, two different methods were used: the *maximal values method* [5,7] and the *constant interval method* [8], which were applied to the experimental peaks and to the best fit ATF. Table 1 shows the values obtained in each case for the kinetic parameters, where the validity of the theoretical substitution carried out may be observed. There is no deviation $> 5\%$, an error inherent to the experimental method.

In order to reaffirm the validity of these ATFs for representing the crystallization reactions of amorphous materials, it is advisable to analyze the constant interval method for determining kinetic parameters. An iterative procedure is used, which gives converging values for $E$, $n$ and $K_0$. It is based on the successive selection of crystallized fraction intervals in which the characteristic function of the model is presumably constant.

Suriñach et al. [9] have proven that the theoretical function which best adapts itself to the experimental results, obtained both in isothermal processes and with continuous heating techniques, is the Johnson–Mehl–Avrami equation

$$\mathrm{f}(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n} \qquad (6)$$

which practically reproduces the experimental plots of $\ln[K_0 \mathrm{f}(x)]$ versus $x$.

Figure 3 shows representations of such plots, derived from applying the method to the ATFs, for alloys M1 and M2, at the different heating rates at which the calorimetric experiments were done. It can be seen that the shape of the functions $\ln[K_0 \mathrm{f}(x)]$ is identical to those derived from the analysis of the experimental peaks, and coincides with the behaviour observed in the abovementioned work by Suriñach et al.

These results seem to imply that the theoretical Johnson–Mehl–Avrami model for the fraction transformed in a crystallization reaction, described by equation (6), can also be expressed, in terms of the crystallization rate, $\mathrm{d}x/\mathrm{d}t$, by a theoretical function of the type

$$\mathrm{d}x/\mathrm{d}t = a\, \mathrm{e}^{-b(t_i-t_0)^2}. \qquad (7)$$

Table 1

Kinetic parameters calculated for alloys M1 and M2, by two methods, using the experimental peaks [a)], and the associated theoretical functions [b)]; $E$ (Kcal/mol), $K_0$ ($s^{-1}$)

| | M1 | | | M2 | | | |
|---|---|---|---|---|---|---|---|
| | $n$ | $E$ | $K_0$ | $n$ | $E$ | $K_0$ | |
| Maximum values | 2.83 | 35.6 | $4.1\times10^{11}$ | 2.63 | 46.8 | $1.4\times10^{16}$ | a) |
| method | 2.61 | 38.7 | $7.4\times10^{12}$ | 2.63 | 46.8 | $1.4\times10^{16}$ | b) |
| Constancy interval | 1.90 | 34.4 | $1.8\times10^{11}$ | 1.78 | 45.2 | $4.0\times10^{15}$ | a) |
| method | 1.87 | 39.1 | $1.4\times10^{13}$ | 2.09 | 46.4 | $1.2\times10^{16}$ | b) |

$M1 = Ge_{0.14}As_{0.43}Te_{0.43}$; $M2 = Cu_{0.10}As_{0.40}Se_{0.50}$.

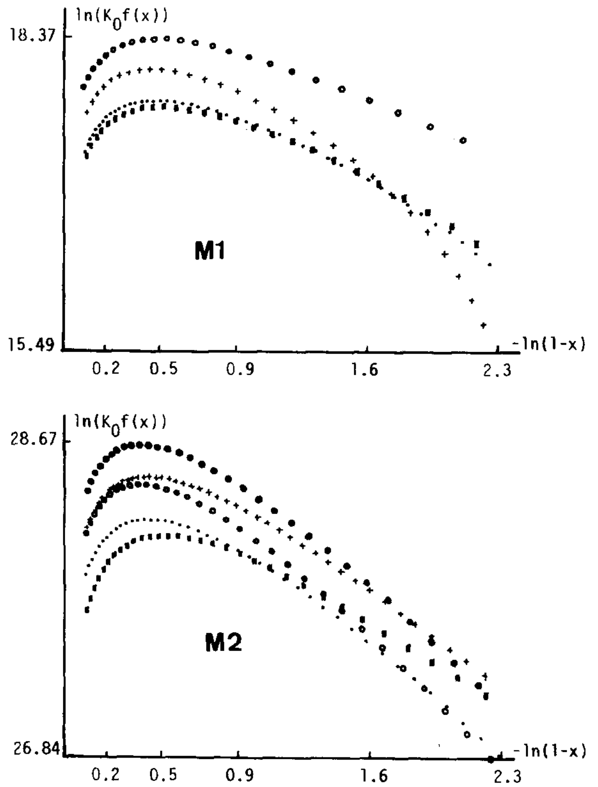

Fig. 3. Representation of ln $[K_0 f(x)]$ versus $-\ln(1-x)$, deduced from the associated theoretical functions for two glassy alloys at the experimental heating rates. ■, 2 K/min; •, 4 K/min; +, 8 K/min; ●, 32 K/min.

## 3. Resolving for overlapping peaks

Once the mathematical function representing one exothermic crystallization peak is found, the solution for two overlapping peaks is simple. Let us, in effect, consider an experimental curve such as the one given in figure 4, the result of two crystallization reactions which overlap in a certain interval of temperature (time). The experimental measurement of the ordinate, in such an interval, is the sum of those supplied by both processes, and the object is to find the fraction corresponding to each individual reaction.

The predominant peak is chosen, a fact which is only relevant in deciding in what order to apply the numerical method described forthwith. In the example given, this peak would be the first (I). According to the formal expression of the ATF, we can assume that: (a) the abscissa of the maximum for peak II, $t_2$, was not altered by reaction I, although the apparent maximum value, $y_2$, will generally increase; and (b) the influence of peak II on peak I will never make the real maximum value of the latter be located to the right of the position, $t_1$, of the apparent maximum, $y_1$. The symmetry of the ATF with peak II makes it possible to state that the reaction represented by this peak will extend, ahead of $t_2$, up to an amount equal to

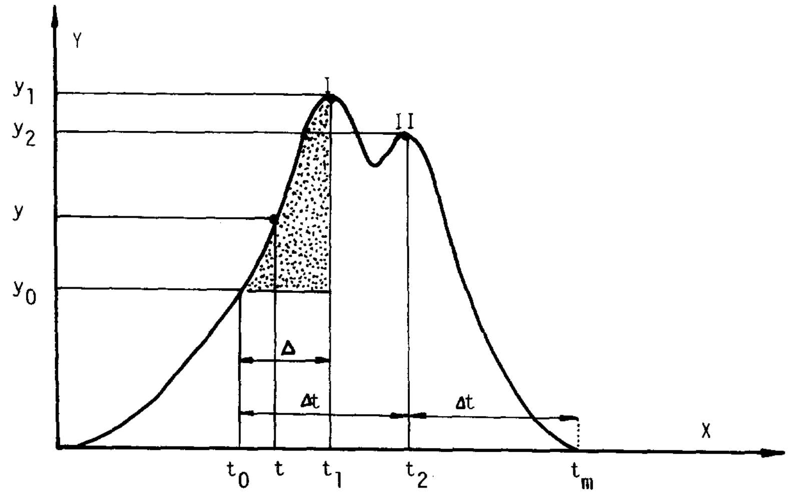

Fig. 4. Hypothetical experimental curve with two overlapping peaks. Dot-shaded area represents the region where real maximum of the first process is located.

Table 2
Area of the experimental curve and the associated theoretical functions (mcal) and relative error of the approximation carried out

| | $A_{exp}$ | $A_1$ | $A_2$ | $A_1+A_2$ | $\epsilon_r$ |
|---|---|---|---|---|---|
| M3 | 195.99 | 97.99 | 88.36 | 186.35 | 0.05 |
| M4 | 156.98 | 53.72 | 97.98 | 151.70 | 0.03 |

M3 = $Cu_{0.05}As_{0.50}Te_{0.45}$; M4 = $Cu_{0.15}As_{0.40}Te_{0.45}$.

$\Delta t = t_m - t_2$, which determines an abscissa interval, $\Delta = t_1 - t_0$, to the left of the apparent maximum value of the first peak, the ordinates of which are the result of the overlapping of the first reaction with the beginning of the second. This overlapping means that the real maximum value of the first process will necessarily be located in one of the abscissas of interval $\Delta$, and that it must be between $y_0$ and $y_1$. Let us call the position and value of the maximum $t$ and $y$, respectively; in this case the experimental data from the beginning of the experimental curve up to $t$ belong to the first reaction, with no interference due to the second, and can therefore be used to make a least squares fit to an ATF, according to the method described in the preceding section, representing the afore-mentioned reaction:

$$f_1(t) = y\, e^{-b_1(t_i - t)^2}, \tag{8}$$

where $b_1$ is the parameter resulting from the adjustment.

By subtracting the above function from the experimental curve, a *residual curve* is obtained, which is related only to the second crystallization reaction, and which makes it possible to calculate, by the same least squares procedure, the ATF for this second crystallization reaction:

$$f_2(t) = y_2'\, e^{-b_2(t_i - t_2)^2}, \tag{9}$$

$y_2'$ being the corresponding maximum.

The experimental curve was thus resolved into two peaks, each representing an individual crystallization reaction, and to which the pertinent techniques can be applied in order to calculate the kinetic parameters.

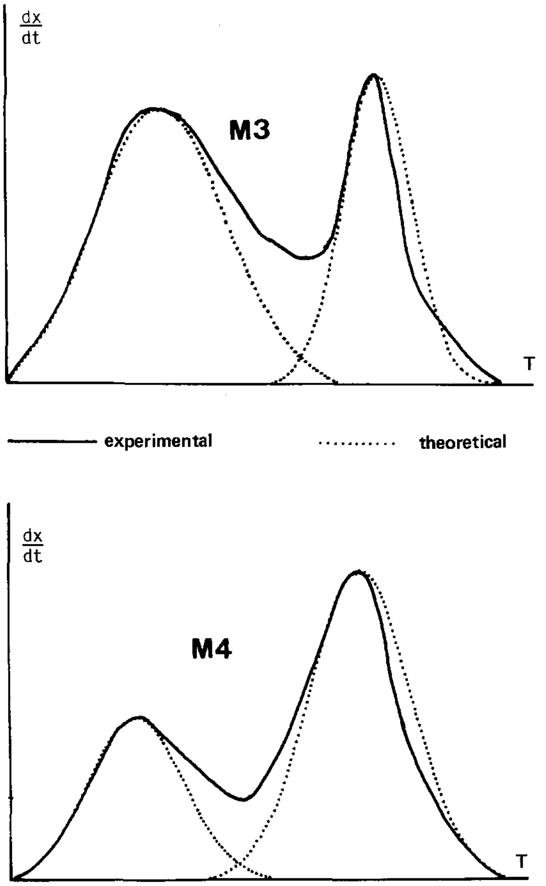

Fig. 5. Theoretical solution of two superposed peaks obtained for two amorphous alloys. M3 = $Cu_{0.05}As_{0.50}Te_{0.45}$; M4 = $Cu_{0.15}As_{0.40}Te_{0.45}$.

The above reasoning is based on the knowledge of point $(t, y)$, which identifies the real maximum of the first peak. However, the only thing we know is that it is located within the area limited by intervals $[t_0, t_1]$ and $[y_0, y_1]$ and the experimental curve itself. By applying the described technique to each of the experimental points in this area, a pair of AFTs will be obtained in each case. $A_{exp}$, $A_1$ and $A_2$ being, respectively, the areas enclosed by the experimental curve and the above mentioned AFTs, the quadratic difference between the areas

$$D = \left(A_{exp} - A_1 - A_2\right)^2 \tag{10}$$

Table 3
Kinetic parameters calculated for alloys M3 and M4 using graphic solutions [a)] and associated theoretical functions [b)]; $E$ (Kcal/mol), $K_0$ ($s^{-1}$)

| Alloy | Stage | Maximum values method | | | Constancy intervals method | | |
|---|---|---|---|---|---|---|---|
| | | $n$ | $E$ | $K_0$ | $n$ | $E$ | $K_0$ |
| M3 | I b) | 1.41 | 46.3 | $2.3\times10^{19}$ | 1.92 | 44.3 | $2.0\times10^{18}$ |
| | a) | 1.03 | 49.2 | $5.0\times10^{20}$ | 1.98 | 48.6 | $1.2\times10^{20}$ |
| | II b) | 2.77 | 51.8 | $2.4\times10^{20}$ | 1.87 | 58.8 | $3.3\times10^{23}$ |
| | a) | 2.98 | 49.2 | $2.2\times10^{19}$ | 1.83 | 57.7 | $1.2\times10^{23}$ |
| M4 | I b) | 1.43 | 49.6 | $5.0\times10^{20}$ | 1.90 | 47.7 | $5.2\times10^{19}$ |
| | a) | 1.23 | 50.6 | $1.5\times10^{21}$ | 1.92 | 47.8 | $4.5\times10^{19}$ |
| | II b) | 1.98 | 43.6 | $4.0\times10^{16}$ | 1.89 | 43.6 | $4.0\times10^{16}$ |
| | a) | 1.95 | 44.6 | $1.3\times10^{17}$ | 1.77 | 52.2 | $2.3\times10^{20}$ |

can be written as follows:

$$D = \tau \sum_{i=1}^{N} \left[ y_i - y\, e^{-b_1(t_i - t)^2} - y_2'\, e^{-b_2(t_i - t_2)^2} \right]^2, \tag{11}$$

where $\tau$ is the abscissa interval separating the experimental values, $t_i$. The pair of values $(t, y)$, to which the above minimum quadratic difference corresponds, defines the two Gaussian functions that resolve the overlapping DSC peaks.

The method was applied to two semiconducting glassy alloys, $Cu_{0.05}As_{0.50}Te_{0.45}$ (M3) and $Cu_{0.15}As_{0.40}Te_{0.45}$ (M4), the thermograms of which exhibit multiple peaks. Figure 5 shows these experimental peaks, for a heating rate of 16 K/min, together with the calculated ATFs which resolve them. Table 2 shows the experimental areas and those enclosed under each ATF, as well as the relative error estimated for the approximation, for the calorimetric experiment carried out at a heating rate of 8 K/min.

The crystallization kinetics of both ATFs were analyzed using the two methods described above, and the values obtained in both cases are shown in table 3. These values were also calculated for the same alloys, using the same techniques, through a classical method for graphically resolving overlapping peaks.

## 4. Conclusions

The Gaussian function deduced in this work has proven to be useful for substituting the single peak of a monophase crystallization reaction. The same information on the crystallization kinetics is basically obtained by using the experimental peaks as through the theoretical function.

When the amorphous-crystal transformation supplies DSC thermograms with two overlapping peaks, the previous result makes it possible to resolve them into two Gaussian functions and to calculate the kinetic parameters which describe each of the overlapping reactions. If both reactions are controlled by the same kind of mechanisms (long-range diffusion or interfacial rearrangement), the information obtained through the associated theoretical functions makes it possible to interpret their respective kinetics correctly. When crystallization is more complex, both control mechanisms coexist, and where both surface and internal crystallization could occur simultaneously, the kinetic results obtained from the Gaussian functions must be considered just as doubtfully as those obtained from the experimental curve itself.

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