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KINETICS OF PHASE TRANSFORMATIONS IN AMORPHOUS MATERIALS BY DSC. PART II

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ABSTRACT

The theoretical models described in Part I of this series (Thermochim Acta , 131 (1988) 211) were used to determine the crystallization kinetics of amorphous $CdGeAs_2$ Implementation of correction techniques were found to be essential to reduce the data to the properties of isolated material and eliminate errors introduced by the DSC device itself These corrections are discussed in detail for both the Perkin Elmer DSC7 (Perkin Elmer Corporation, Norwalk, CT, U S A) and the DuPont 1090 DSC (E I DuPont de Nemours Inc , Wilmington, DE, U S A), and the calculated kinetic parameters are compared for the two devices The effect of the use of bulk samples as opposed to many fine granules is also discussed

1 INTRODUCTION

Although a great deal of theoretical work has been produced on obtaining activation energies of crystal growth via isothermal studies, as well as multiple and single scan heating rate studies, the experimental considerations lending reliability to these values [1–3] have not been adequately explored Important corrections to the information obtained on the experimental DSC trace itself are often overlooked in the mistaken belief that the use of sophisticated instrumentation coupled with a number of “black box” software programs yields valid results

It is the intent of this paper to scrutinize the operation of the two most popular DSC instruments (DuPont and Perkin Elmer) and determine what corrections need to be made, and what factors should be accounted for, in order to obtain meaningful data from the devices The transformation of interest for this study is the crystallization of amorphous $CdGeAs_2$, which

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should typify the rapid and highly exothermic crystallization transformation of many amorphous semiconducting alloys and metallic glasses

2 SAMPLE PREPARATION

Stoichiometric amounts of elemental Cd, Ge and As were sealed in a 6 mm diameter fused silica tube under a vacuum of ~ 10^{-7} torr The tube was suspended from a Kanthal wire in an SiC heating element furnace held at 800 °C for ca 24 h, in order to melt and homogenize the batch constituents The compound was then slowly cooled, separated from its container, crushed using a clean mortar and pestle, and then resealed in individual 2-mm ID fused silica tubes under similar vacuum conditions

The individual tubes were once again suspended in the furnace at 800 °C for ca 24 h The Kanthal wires were then cut, allowing the tubes to plunge into a glycol/water solution at ca −20 °C Processing in this manner yielded ampoules of $CdGeAs_2$ in the vitreous form, confirmed by X-ray diffraction and reflected light optical microscopy under crossed-polarized light

Numerous small particles of amorphous $CdGeAs_2$ of sizes smaller than 40 mesh and larger than 70 mesh were used as reactant in the hermetically sealed DSC sample capsule All experiments on both devices used granules originating from the same 2-mm fused silica tube during a single quenching event Both instruments were temperature calibrated using high purity tellurium with a melting point of 449 5 °C

3 ISOTHERMAL STUDIES

3 1 Anomalies at the junction

The careful matching of heat capacities is especially important in isothermal studies Since the dependence of the heat capacity term is proportional to dT_r/dt (eqn (1) in Part I of this series [4]), the contribution of this term will go from some finite value to zero as the rapid temperature rise converts to isothermal at the junction This in turn will cause a distortion in the initial region of the crystallization exotherm

An illustration of errors introduced due to heat capacity mismatch in the DuPont 1090 apparatus is shown in Fig 1, which is a trace of an isothermal crystallization treatment of amorphous $CdGeAs_2$ An excessive mass of reactive material was used in the sample capsule, and the reference capsule was left empty During heatup, $T_s - T_r$ is negative (endothermic) which is expected, since the more massive sample required more heat to raise its temperature (greater heat capacity) than the reference, and thus lagged

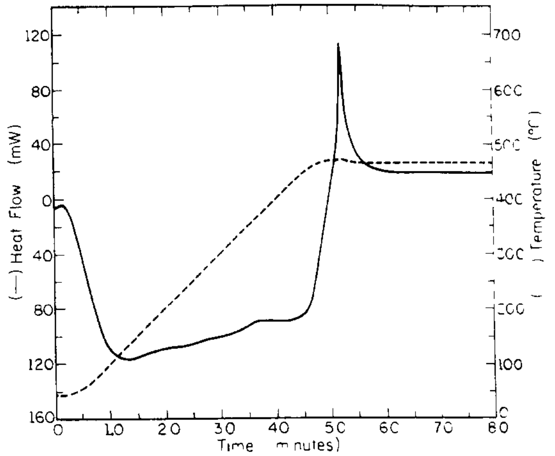

Fig 1 DuPont 1090 DSC trace of isothermal devitrification of CdGeAs$_2$ The extended endotherm between 0 5 and 5 0 min is a result of the heat capacity mismatch between the empty reference capsule and the sample capsule containing granules of the amorphous alloy

behind the reference in temperature This difference, after ca 1 5 min, reached an approximate equilibrium, which would define the baseline for a heating rate investigation If, at any point the heating rate halts to isothermal, this temperature difference will relax to zero as the temperature of the sample catches up However, this relaxation of the temperature difference will be superimposed upon the onset of the crystallization exotherm, and hence will distort the initial shape of the peak

The Perkin Elmer system, although capable of a more abrupt heating rate to isothermal change, has what may be a more severe problem at the junction Since the sample and reference capsules are isolated, the abrupt change in heating schedule may not be exactly reproduced in each of the isolated chambers containing sample and reference capsules, hence the null balance is temporarily lost The difference in measured temperature of sample and reference at the junction may be due to variations in heating element behavior, different heat capacities, or slight differences in capsule geometry or position, causing different rates of heat transfer Notwithstanding these factors, it takes ca 17 s for the system to regain its temperature balance, and the data taken during that time is considered to be uninterpretable [5]

3 2 The subtraction method

A typical isothermal DSC trace for the DuPont instrument is marked with circles in Fig 2 If all the deviations from a straight baseline are solely due to transformations, i e the glass transition t_g and devitrification, then a straight baseline should be produced when the sample is again cycled

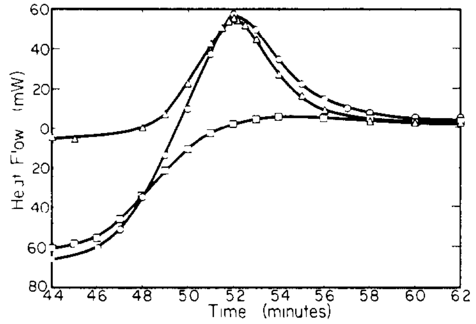

Fig 2 Heat flow versus time plot depicting the subtraction method for isothermal runs on the DuPont 1090 (but applicable to either device) (o) DSC trace of the crystallization event, representing the material's behavior plus device anomalies, (□) second run of the same sample (now crystallized) and reference through the same temperature program, representing solely device anomalies, (△) subtraction of the first two, representing the crystallization event devoid of device error

through the same thermal treatment This assumes, of course, that no further transformation occurs in the sample on the second run

The curve marked with squares in Fig 2 shows a typical plot of a second run, and as can be seen, it displays anything but a linear baseline To determine whether further transformations were taking place, the sample was cooled and re-exposed to the same thermal schedule a number of times It was found that all successive runs after the first were exactly reproducible on the DuPont 1090 and on the Perkin Elmer DSC7 (reasonably reproducible on the DSC7 near the junction)

What is observed, therefore, must be due to the anomalies at the junction previously discussed, and other baseline nonlinearity caused by the instrument All of these may be referred to as "device error," which distorts the actual shape and size of the transformation curves Fortunately, so long as sample and reference positions are in no way altered, the fact that this device error can reproduce itself exactly makes it reasonable to simply subtract it

The curve marked by triangles in Fig 2, which is the subtraction of the square coded curve from the circle coded curve, is representative of solely "material" properties A similar second temperature cycle was recorded for every isothermal run in our work (for both instruments), and the curves were subtracted

Although not as crucial, second runs were recorded and subtracted for all heating rate studies as well This was done to eliminate any baseline drift

3 3 Isothermal temperature correction for the DuPont 1090

During the beginning of the isothermal portion of a DuPont DSC trace, the temperature of the sample T_s is still relaxing to the designated isother-

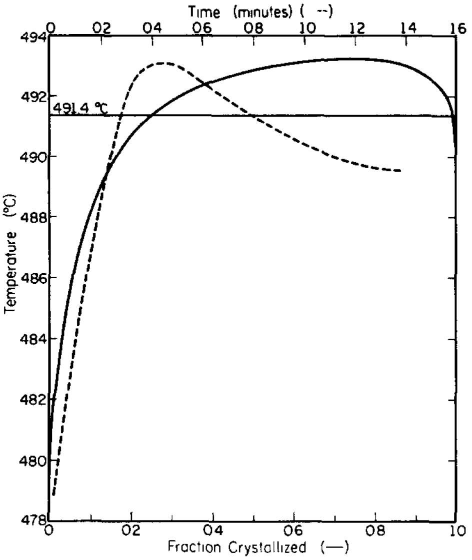

Fig 3 Method for determining weighted average isothermal temperature on the DuPont 1090 An isothermal transformation programmed to occur at 500 ° C is actually exposed to temperatures as a function of time depicted by the broken line From the fraction crystallized versus time data, this temperature schedule was converted to temperature versus fraction crystallized, and the area under this curve was integrated to obtain a weighted average temperature of 491 4 ° C

mal level (section 2 6 of Part I [4]) In addition, the exothermic nature of the transformation alters the sample temperature, which is uncompensated by the device (section 2 4 of Part I [4]) These temperature variations introduce inaccuracy when manipulating the data using standard mathematical methods for isothermal runs (sections 3 1 and 3 2 of Part I [4]), which require input of an invariant isothermal temperature

A corrected value of T_s must be established by determining some "averaging" isothermal temperature which the sample experiences during the transformation period At first glance, the most straightforward method of correction is to determine the average isothermal temperature over the time in which the transformation took place [6] Upon further consideration however, this method would weigh equally temperatures at those times in which the reaction is just beginning or near termination, with those corresponding to when the reaction is proceeding at its maximum rate A more accurate description would be to weigh more heavily the temperatures at those times in which the greater majority of the reaction took place

Since we have data relating the fluctuation in temperature in the isothermal region as a function of time (broken line in Fig 3), as well as fraction crystallized data as a function of time, we can combine the two to plot sample temperature as a function of fraction crystallized (solid line in Fig 3) In this representation, temperatures at which the transformation rate was slow are represented by small a fraction transformed, whereas temperatures at which the transformation rate was rapid is represented by a large fraction transformed Therefore, integrating the area under this curve from $F = 0$ to $F = 1$ will yield a "weighted" average isothermal temperature For this example, the isothermal temperature the device eventually relaxed to was 489 6 ° C, the average isothermal temperature (during the period from the onset to the termination of the crystallization peak) was 478.3° C, and the "weighted" average temperature was 491 4° C The weighted isothermal temperature was used in all calculations for isothermal runs on the DuPont 1090 DSC

3 4 Isothermal devitrification of $CdGeAs_2$ on the Perkin Elmer DSC7

We have found that in isothermal studies of amorphous $CdGeAs_2$ with the Perkin Elmer device, two overlapping exothermic peaks appeared on the generated DSC traces We have developed a method (section 3 2 of Part I [4]) for determining separate activation energies and crystallization mechanism constants for the two superimposed DSC transformation peaks

The experimental exotherms for this isothermal study are shown in Fig 4 The five SAS determined coefficients along with the measured integrated areas under each experimental peak, and the mean square error (MSE) between eqn (9) of Part I [4] and the DSC trace are shown in Table 1 The correlation of the DSC output to theory via the five coefficients was excellent (see fig 5 of Part I [4]) at all temperature ranges except for 500, 505, and 510° C In this temperature range, the two peaks were so close together that curve fitting by the SAS program became difficult.

An Arrhenius plot (logarithmic from of eqn (5) of Part I [4]) of the first (earliest) and second peak, using the values of k_1 and k_2 and temperature

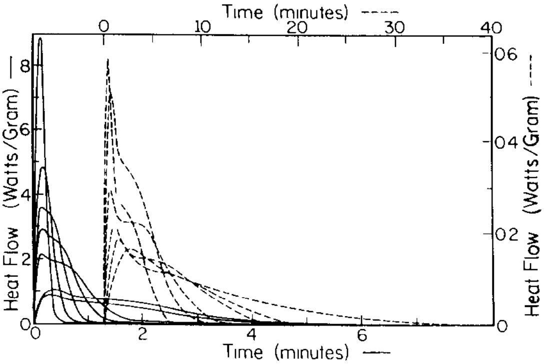

Fig 4 Output of Perkin Elmer DSC7 for isothermal devitrification of $CdGeAs_2$ Curves from left to right represent exotherms from experiments going from highest (510° C) to lowest (450° C) isothermal temperature, respectively

TABLE 1

SAS calculated peak areas, rate, and mechanism constants

T(°C)	k_1	n_1	k_2	n_2	A_1	A_T	MSE [a]
450	0 630	2 119	0 022	1 498	3 052	17 892	0 0120
455	0 246	2 143	0 027	1 672	1 327	8 788	0 0009
460	0 475	1 821	0 026	1 821	2 213	12 906	0 0003
465	1 408	1 740	0 061	1 758	0 966	7 609	0 0006
470	1 172	1 621	0 076	1 890	3 489	15 810	0 0080
475	2 470	1 663	0 144	1 812	2 330	8 799	0 0075
480	4 814	1 924	0 294	1 775	3 071	19 251	0 0200
485	6 336	1 913	0 381	1 582	1 278	10 350	0 0088
490	26 079	1 922	1 565	1 808	1 592	16 005	0 1000
495	33 792	1 968	2 731	1 898	1 332	10 145	0 0070
500	754 624	3 114	4 938	1 791	0 636	15 804	0 6360
505	0 0	–	10 043	1 793	0 0	8 298	0 4200
510	0 0	–	33 420	2 040	0 0	12 655	0 6300

[a] Mean square error between eqn (9) of Part I and the DSC trace

(minus temperature calibration) listed in Table 1 are shown in Fig 5 A least-squares fit of this data yields an activation energy of 112 4 kcal mol^{-1} for the first peak and 136.64 kcal mol^{-1} for the second peak The predicted pre-exponential factors for the two peaks differed by six orders of magnitude, $k_{0,1\text{st}} = 4\ 44 \times 10^{33}$, $k_{0\ 2\text{nd}} = 4\ 51 \times 10^{39}$ The lower activation energy for the first peak implies that there is a lower kinetic barrier for the first reaction to take place, and thus it is initially the favored transformation, as observed The larger pre-exponential factor (often termed the frequency factor) for the second peak implies that the jump rate of atoms across the glass–crystal interface is large, so that if the kinetic barrier is surmountable,

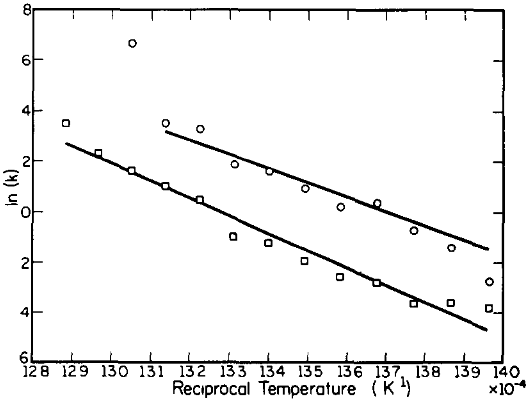

Fig 5 Arrhenius plot of k_1, k_2, and temperature data from Table 1 (○) First (earliest) peak, (□) second peak, (———) least-squares fit to the data The data point at 500 °C for the first peak was ignored in the least squares estimate

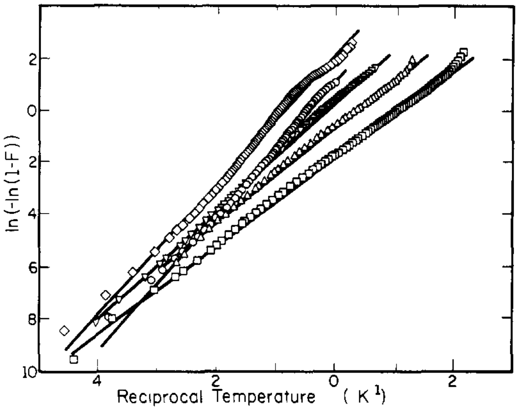

Fig 6 Avrami plots of the fraction crystallized data from an isothermal study of $CdGeAs_2$ on the DuPont 1090 DSC (◇) 490 4 °C, (○) 480 9 °C, (▽) 470 2 °C, (△) 458 9 °C, (□) 449 6 °C

a large volume of crystalline phase will form per unit time via the second reaction

The fact that the first peak terminates without complete crystallization of the glass implies that this reaction may be starved of some particular element required to continue the transformation, i e is diffusion limited This transformation has been confirmed in other work [6] to be the precipitation and limited growth of crystalline germanium (doped with cadmium and arsenic impurities) This metastable phase acts as heterogeneous nucleation sites for the subsequent growth of chalcopyrite $CdGeAs_2$, represented by the later, larger exotherm

3 5 Isothermal devitrification of $CdGeAs_2$ on the DuPont 1090 DSC

Remarkably, the superimposed DSC exotherms shown by the Perkin Elmer DSC7 were not observed on the DuPont 1090 DSC (although the

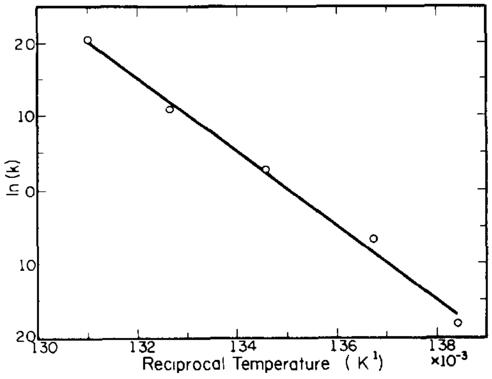

Fig 7 Arrhenius plot of data from Table 2 to determine the activation energy of crystallization for $CdGeAs_2$ using the DuPont 1090 DSC

TABLE 2

Slopes and intercepts from Avrami plot for DuPont 1090 isothermal data

Corrected temperature (° C)	ln k	n [a]
490 4	2 05	2 42
480 9	1 08	2 58
470 2	0 27	2 08
458 5	−0 68	1 82
449 6	−1 81	1 69

[a] Mechanism constant

DSC trace at the lowest isothermal temperature of 449 6 ° C showed evidence of splitting into two peaks) The data were thus manipulated using the standard procedures discussed in section 3 1 of Part I [4] Values of k and n were obtained from a plot of the logarithmic form of the Avrami expression (Fig 6) and are listed in Table 2

A plot of these data fit to the logarithmic form of the Arrhenius expression (Fig 7) yielded an activation energy of 99 81 kcal mol^{-1}

4 HEATING RATE STUDIES

4 1 Heat capacity correction to devitrification reaction

As can be seen from Fig 8, which is typical for both devices, the baseline after the end of the transformation is not the same as before its onset (for both devices) This shift is not due to any anomaly in the apparatus, but rather to the fact that the sample is a transforming phase while the reference is not The ordered crystalline state of the sample after the transformation requires less heat than the amorphous state to increase its temperature, thus the baseline shifts

A correction is needed to acount for the variation in the baseline during the exothermic glass-to-crystal transformation We assume that the baseline changes linearly with the volume fraction of glass transformed to the crystalline state This follows from the location of the baseline being a function of the sample heat capacity (in relation to the reference), and the sample heat capacity will vary linearly with a linear variation in composition from amorphous to crystalline states

Fraction crystallized versus time data can be generated via integrating partial areas of the DSC peak as before Although this F vs t data will not be exact since they have not been corrected for this change in heat capacity, it will be acceptably close These data can then be used to convert the baseline versus fraction crystallized data to baseline versus time data (broken line in Fig 8) These data, representing heat capacity alteration during the

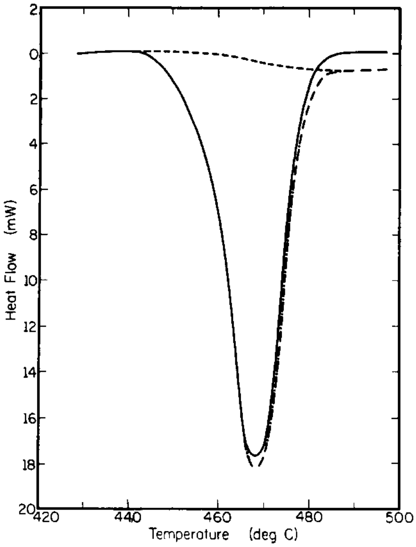

Fig 8 Correction technique for heat capacity change in the sample while transforming from the amorphous to crystalline state during a heating rate study (either device) (– –) experimentally determined DSC exotherm, (------) calculated change in heat capacity with temperature (see text), (———) corrected DSC exotherm obtained by subtraction of the first two lines

ordering of the amorphous sample, may then be subtracted from the original DSC data to obtain a corrected peak, as shown as a solid line in Fig 8 This correction was made on all data generated from DSC heating rate studies on both devices

4 2 Heating rate study of $CdGeAs_2$ on the Perkin Elmer DSC7

We have studied the crystallization of amorphous $CdGeAs_2$ using DSC at various heating rates, which generated the fraction crystallized versus time data plotted as circles in fig 9 The lines in the figure represent data generated through eqn (15) in Part I [4] using the determined kinetic parameters via the previously described data manipulation The values of these parameters are given in Table 3

From Table 3, the average value of activation energy for crystallization is 113 36 kcal mol^{-1} with a standard deviation of 17 98 kcal mol^{-1} The average mechanism constant is 1 35 with a standard deviation of 0 33

The values of these kinetic parameters were very sensitive to the choice of onset temperature Thus, the variation in kinetic data for differing heating rate in Table 3 may be partly attributable to the choice of the onset temperature Onset temperatures were chosen at the point where the baseline first deviated into the peak On some DSC traces the location of this temperature was obvious whereas on others it was not We chose the range

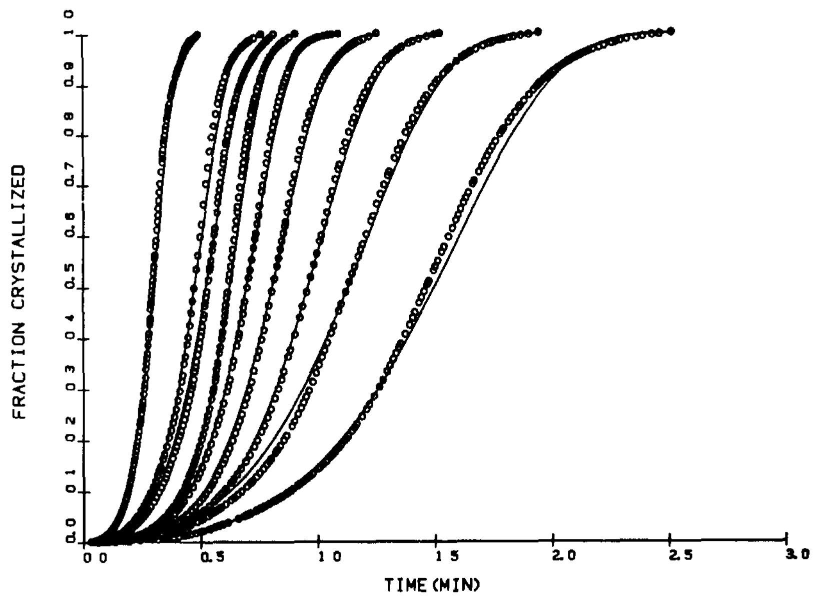

Fig 9 Fraction crystallized versus time data obtained from experimental Perkin Elmer DSC7 traces The curves shown by solid lines were obtained by inserting the values of E_c, n, A_0 T_{onset}, and ϕ in eqn (15) of Part I [4] Heating rates vary, from left to right, from 150 to 15 °C min^{-1}

of temperatures which could be reasonably taken as the onset and averaged the resulting kinetic data from these choices The plus/minus deviations indicated in Table 3 represent the scatter in these data

The lower activation energies at the more rapid heating rates may be explained by considering that reaction zones within the material may have been forced to a higher temperature (due to the exothermic nature of the

TABLE 3

Calculated activation energies and mechanism constants for heating rate crystallization using the Perkin Elmer DSC7

Heating rate (°C min^{-1})	Activation energy (kcal mol^{-1})	Mechanism constant n
15	116 32±7 99	1 73±0 18
20	111 06±3 53	1 62±0 04
30	118 95±4 68	1 26±0 16
40	123 73±6 88	1 50±0 15
50	123 66±1 40	1 28±0 09
60	123 54±0 22	1 27±0 00
70	127 66±1 40	0 68±0 06
80	106 41±5 09	1 10±0 09
150	68 96±3 28	1 72±0 20

TABLE 4

Calculated activation energies and mechanism constants for heating rate crystallization using the DuPont 1090 DSC

Heating rate (°C min^{-1})	Activation energy (kcal mol^{-1})	Mechanism constant n
20	116 25 ± 7 93	1 59 ± 0 26
30	119 15 ± 5 13	1 41 ± 0 18
40	106 87 ± 11 61	1 67 ± 0 38
50	106 29 ± 4 05	1 48 ± 0 11
60	90 72 ± 5 91	1 70 ± 0 18
70	83 87 ± 4 99	1 75 ± 0 17
90	35 93 ± 6 12	2 19 ± 0 35

reaction) which was not compensated for adequately by the Perkin Elmer device, thus speeding up the reaction The device would record an abnormally rapid transformation rate for a given heating rate which would cause us to calculate an activation energy which was too low Further evidence for an avalanche effect with the Perkin Elmer DSC7 is provided in section 5 of this work, as well as section 2 4 of Part I [4]

4 3 Heating rate study of $CdGeAs_2$ on the DuPont 1090

Fraction crystallized data from heating rate traces on the DuPont 1090 DSC were fitted to eqn (15) Part I [4] The activation energies and mechanism constants for these traces are given in Table 4

4 4 Discussion

The agreement between the DuPont 1090 and the Perkin Elmer DSC7 activation energies and mechanism constants for heating rate studies was remarkably good for the lower heating rates, but the activation energies fell more rapidly for the DuPont device at higher heating rates (Fig 10) This behavior is clearly due to the design of this DSC which acts to resist transformation avalanche Since the reaction proceeds at temperatures much higher than those programmed, and thus proceeds more quickly, and we erroneously use the programmed temperature values in our calculations, we predict a kinetic barrier to crystallization which is too low (notably 35 93 kcal mol^{-1} in the 90 °C min^{-1} case on the DuPont 1090)

It should be noted that the values of activation energy fell at higher heating rates on the Perkin Elmer DSC7 as well, indicating that the device could not completely compensate for the "self-feeding" nature of the transformation either, although it appears to do a better job than the DuPont 1090

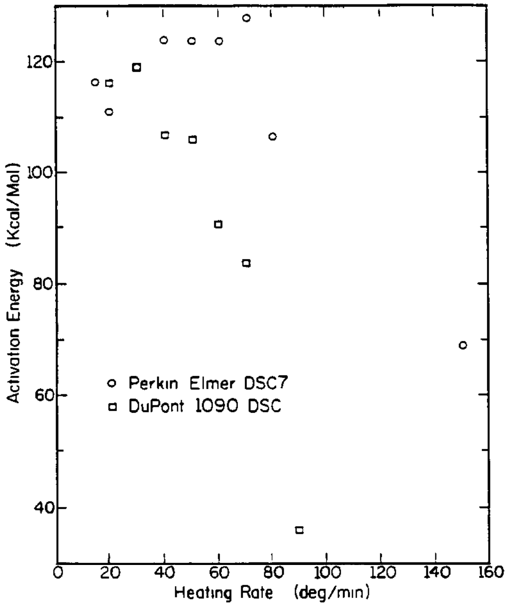

Fig 10 Activation energy of crystallization of $CdGeAs_2$ at various heating rates as determined by two different DSC devices

In the isothermal studies on the Perkin Elmer DSC7, we observed that the isolated peaks merged closer and closer together with increasing isothermal temperatures, until ca 500 °C when they were indiscernible to the SAS program and ca 510 °C when they were indiscernible to the eye, and appeared as one smooth peak This implies that, at higher isothermal temperature, the reaction corresponding to the second peak dominates and (the thermal effect of) the reaction corresponding to the first peak becomes imperceptible

This consideration provides a basis to explain why double peaks are not observed on the DuPont 1090 instrument above isothermal temperatures of 450 °C As the reaction initiates, the sample temperature rises quickly on a result of the heat released, since this heat is not removed by the device. Thus, the dominant reaction mechanism of the transformation quickly alters to the higher-temperature regime, in which the second peak predominates and the first peak is suppressed out of visual existence

We further consider this to be the explanation as to why only single exotherms were observed on the Perkin Elmer device in the heating rate studies The fact that the sample temperature was programmed to increase at a known rate tended to mask the first exotherm at all but very slow heating rates, since the sample was exposed for an inadequate time to the lower crystallization temperature Double peaks were observed on the Perkin Elmer device for heating rates of 15 °C min^{-1} and lower, and on the DuPont device for heating rates of 5 °C min^{-1} and lower

5 EFFECT OF SAMPLE PARTICLE SIZE AND DISTRIBUTION

To determine the effect of sample particle size on the behavior of the DSC exotherm, glassy $CdGeAs_2$ was crushed using a clean mortar and pestle and passed through 16 (1 18 mm diameter), 30 (0 60 mm), 40 (0 425 mm), and 70 (0 212 mm) mesh screens

The total mass of the particles making up each sample was 8($\pm$1) mg To make up that mass, fewer particles were used with increasing particle size, in the 16 + mesh case, a single particle was used Each sample was subjected to an identical thermal treatment of 100 °C min^{-1} to 400 °C, and 30 °C min^{-1} through its crystallization temperature range

The experiment was repeated several times to guarantee reproducibility Partial areas of each peak were divided by the entire area to obtain the fraction crystallized as a function of time data Typical results for the DuPont 1090 and the Perkin Elmer DSC4 (predecessor to the DSC7) are shown in Fig 11 For both instruments, the 70 + and 40 + mesh samples demonstrated nearly identical "S"-shaped curve, whereas the 30 + sample deviated slightly and the 16 + mesh sample deviated substantially

A number of observations may be made to explain these results The samples with the most intimate contact with their container will have their transformations most accurately recorded since the effects of heat transfer lag to the temperature measuring device (thermocouple or platinum resistance thermometer) are minimized Smaller particles will have more intimate contact with the base of the capsule than fewer, larger particles The lower values of *F* at earlier times for the 16 and 30 mesh samples are taken as examples of a time lag for the temperature measuring device detecting the heat of the transformation in bulkier samples

The sharp crossover of the 16 mesh sample (over the smaller particle sizes) to larger fraction crytallized is interpreted as a typical result in highly

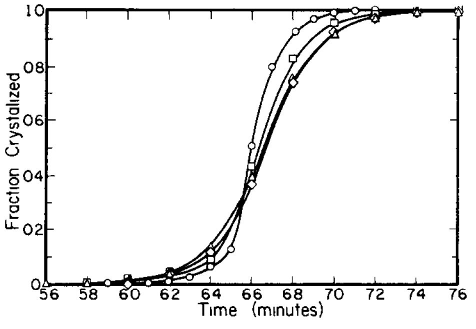

Fig 11 Fraction transformed versus time for samples of different sizes on the DuPont 1090, and Perkin Elmer DSC4 (○) Granules of size greater than 16 mesh, (□) particles between 16 and 30 mesh, (△) particles between 30 and 40 mesh, (◇) granules between 40 and 70 mesh See text for discussion

exothermic transformations in which the reaction avalanches, or “feeds on itself ” Larger granules have a smaller surface-to-volume ratio, and the heat released due to the transformation will be less apt to dissipate, and thus contribute more toward temperature rise The generation of heat along the growing glass–crystal interface raises the temperature of the granule, causing it to transform more quickly, which in turn raises the temperature of the sample, causing it to “avalanche” through its crystallization transformation.

It is therefore apparent that smaller particle sizes yield the greatest reproducibility The limitation to this viewpoint is if the crystallite size approaches that of the particle dimensions, or if the reduction in particle size alters the mechanism of crystallization, e g to surface nucleation and subsequent inward growth For the 30 + mesh particle size, evidence provided elsewhere [6] confirms that for CdGeAs$_2$ neither is the case

SUMMARY PARTS I AND II

(1) The basic operating principles of the DuPont 1090 DSC and the Perkin Elmer DSC7 differ The Perkin Elmer apparatus measures the amount of electrical energy required to maintain a null balance in temperature between sample and reference The DuPont device measures the difference in temperature between sample and reference and than converts this information into units of energy

(2) One needs to take care when attempting to obtain meaningful quantitative crystallization kinetic information from the DuPont system, since the device may not maintain a controlled sample temperature when moderately massive samples are used, or when high (70–100 °C min^{-1}) heating rates are used On the other hand, the Perkin Elmer device output does not provide information about the sample temperature, so that one would not know when avalance effects perceptibly alter sample temperatures from the programmed values

(3) All isothermal traces should be run twice, the second time with the fully crystalline form of the sample, and then the second peak is subtracted from the first to isolate properties strictly of the material.

(4) For isothermal crystallization studies on the DuPont 1090 DSC, an estimate of isothermal temperature may be made (as actual sample temperature is recorded on this instrument) since the cell, and sample do not immediately assume a stable temperature after the junction A method for determining the weighted average isothermal temperature was described

(5) Isothermal devitrification studies of amorphous CdGeAs$_2$ on the DuPont 1090 apparatus yielded a single peaked transformation with an activation energy of 99 8 kcal mol^{-1} Studies on the Perkin Elmer device yielded double, superimposed peaks, with isolated activation energies of 112 4 and 136 6 kcal mol^{-1} The single peak on the DuPont instrument was

suspected to be a result of the highly exothermic nature of the transformation raising the temperature of the sample so as to mask the thermal effect of the first reaction The lower value of activation energy for the DuPont isothermal experiments was considered to be a result of the erroneously low recorded isothermal temperatures used in the Arrhenius calculation, which did not represent the actual temperature of the sample during devitrification

(6) Crystallization exotherms should be corrected for the gradual change in heat capacity of the sample as it transforms from the vitreous to the crystalline state

(7) The agreement between the calculated values of activation energy of crystallization via both devices was remarkably close for moderately slow heating rates (ca. 120 kcal mol^{-1}), yet these values decreased at higher heating rates due to uncompensated transformation avalanche The drop in activation energy with increasing heating rate was more severe in the DuPont system

(8) Small granules rather than a single bulk sample (making up the same mass) were found to produce greater reproducibility in generating fraction crystallized versus temperature plots from DSC traces for both instruments

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