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ON THE THERMAL DECOMPOSITION OF K_2PdCl_4 IN A HYDROGEN ATMOSPHERE

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ABSTRACT

The decomposition of single crystals and powders of K_2PdCl_4 in a hydrogen atmosphere was investigated by means of thermogravimetry (TG) at temperatures between 85 and 170°C, and by optical microscopy. The rate of decomposition is controlled by a combined process of nucleation and growth. The activation energy was calculated to be 15.2 ± 0.5 kcal mol^{-1} for single crystals and 13.5 ± 0.4 kcal mol^{-1} for powders. The results are compared with those obtained for K_2PtCl_4.

An attempt was made to explain the differences in the orientation relationships, previously determined by X-ray diffraction, between K_2PtCl_4 and K_2PdCl_4, Rb_2PdCl_4 and K_2PdBr_4 and their decomposition products with a different kinetic behaviour.

INTRODUCTION

As reported earlier[1] single crystals of K_2PtCl_4 and K_2PdCl_4 have been decomposed in a hydrogen atmosphere, according to the reaction $K_2MCl_4 + H_2 \rightarrow 2KCl + M + 2HCl\uparrow$ (M = Pt or Pd) and the orientation relationships between the single crystals and their polycrystalline decomposition products have been investigated[1]. The orientation relationships appeared to be different for both compounds, and no explanation of the observed relationships has been given, in cases where a fitting process, based on the similarity of the inter-atomic or -ionic distances in parallel directions, has failed[2-4]. Because, for the two compounds mentioned above, all corresponding lattice parameters of the crystals involved in the decomposition process are equal to within a few hundredths of an Ångstrom, no explanation could be based on geometrical factors. Therefore, an attempt was made to find an explanation based on differing kinetic behaviour.

The results of the reaction kinetics obtained for K_2PtCl_4 have been reported previously[5]. This paper deals mainly with the reaction kinetics of K_2PdCl_4. The orientation relationships between single crystals of K_2PdBr_4 and Rb_2PdCl_4 and their decomposition products in hydrogen have also been studied. These two salts belong to the same tetragonal space group, but their unit cell dimensions are larger[6]. Preliminary results reveal the same relationships as for K_2PdCl_4.

EXPERIMENTAL

The preparation and the morphology of the single crystals have been described elsewhere[6]. The powders were obtained directly from Drijfhout (Amsterdam) or prepared from the corresponding reagent grade alkali- and palladium halides in acid solution. The diameter of the particles ranged from 1 to 50 μm.

The weight loss of the decomposition reaction of K_2PdCl_4 in hydrogen was measured as a function of time by thermogravimetry in the same way as for K_2PtCl_4[5]; a symmetrical thermobalance was used[7].

The single crystals were examined under a microscope and SEM views were made of the {100} faces of K_2PdCl_4 and K_2PtCl_4. Cross-sections of partly decomposed K_2PdCl_4, Rb_2PdCl_4 and K_2PdBr_4 single crystals, embedded in a two-component resin, were investigated by dark field microscopy.

DECOMPOSITION OF SINGLE CRYSTALS OF K_2PdCl_4

When single crystals of K_2PdCl_4 are heated gradually in hydrogen, black needles develop at the surface and inside the matrix of the crystals at about 80 °C. Each needle arises instantaneously and becomes slowly thicker and longer. These needles, stretching in the ⟨100⟩ directions, are probably due to edge dislocations. Their formation can only be revealed under a microscope and cannot be detected thermogravimetrically.

On further heating at temperatures above 110 °C, the decomposition extends all over the crystal surface. In contrast to the behaviour of K_2PtCl_4, where the reaction progresses with a rather flat interface from the surface into the bulk of the crystal, the reaction interface of K_2PdCl_4 is very irregular (see Fig. 1). A cross-section of a partly decomposed crystal reveals many very thin, irregularly-shaped sheets of decomposed material. These sheets extend from the surface into the bulk of the crystal along (001) planes. By analogy with the formation of the needles, it may be assumed that these thin sheets also develop very quickly. During the reaction process, these sheets grow slowly in the direction of the C-axis and new sheets develop from the crystal surface or from the ends of the thickened reaction layers. Just as for K_2PtCl_4, the porosity of the decomposed region is large, due to a 32% decrease in the volume of the solid state combined with the maintenance of the original external dimensions of the crystal; hence, the gaseous products H_2 and HCl can diffuse freely to and from the reaction interface, and diffusion is not a rate-controlling step. Therefore nucleation and growth of the nuclei are left as possible rate-determining steps. These two steps cannot be separated because both steps occur simultaneously and contribute to the decomposition rate.

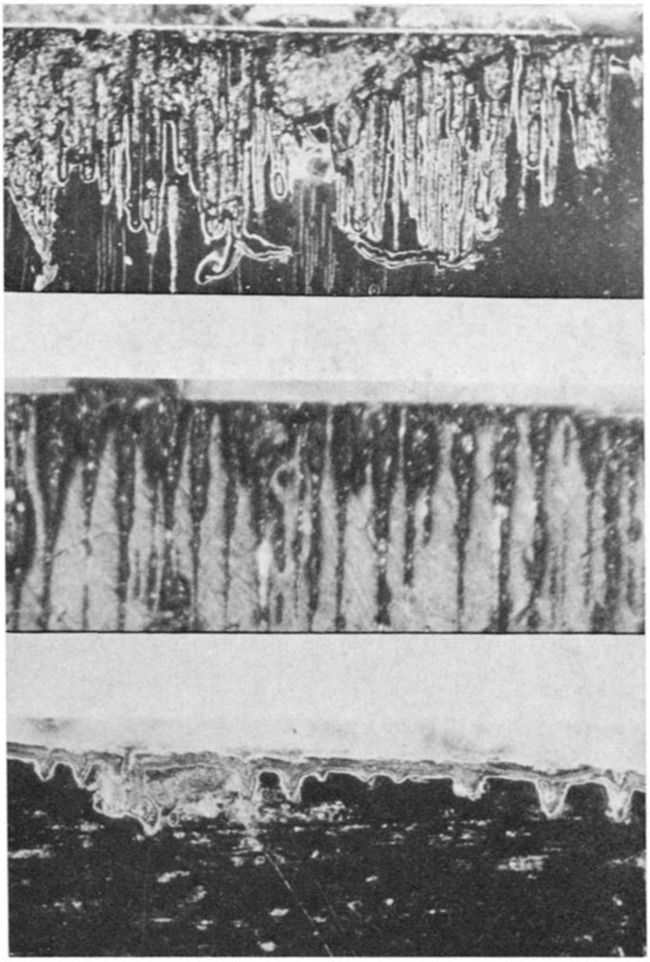

Fig. 1. Cross-sections of partly-decomposed single crystals of K_2PdCl_4 (upper), Rb_2PdCl_4 (middle) and K_2PdBr_4 (lower) parallel to a {100} crystal face with the C-axis horizontal. Magnification 40×.

Calculation of kinetic parameters

At any given moment, the decomposition rate is proportional to the extent of the reaction interface. However, due to its irregular shape, the reaction interface cannot be related directly to the degree of decomposition, as could be done for K_2PtCl_4. In the case of K_2PdCl_4 the reaction interface depends not only on the degree of progress of the reaction, but also on the behaviour of the individual crystal, and on the decomposition procedure followed. Therefore the activation energy of the reaction could not be calculated by comparison of the decomposition rates of different crystals, each of which had been decomposed isothermally at a different temperature. For this reason, a stepwise decomposition procedure was applied to the single crystals to calculate the activation energy. Each step corresponded with a certain reaction temperature. After each 10% of decomposition, in which about two steps at different temperatures were measured, one step was carried out at a fixed chosen reference

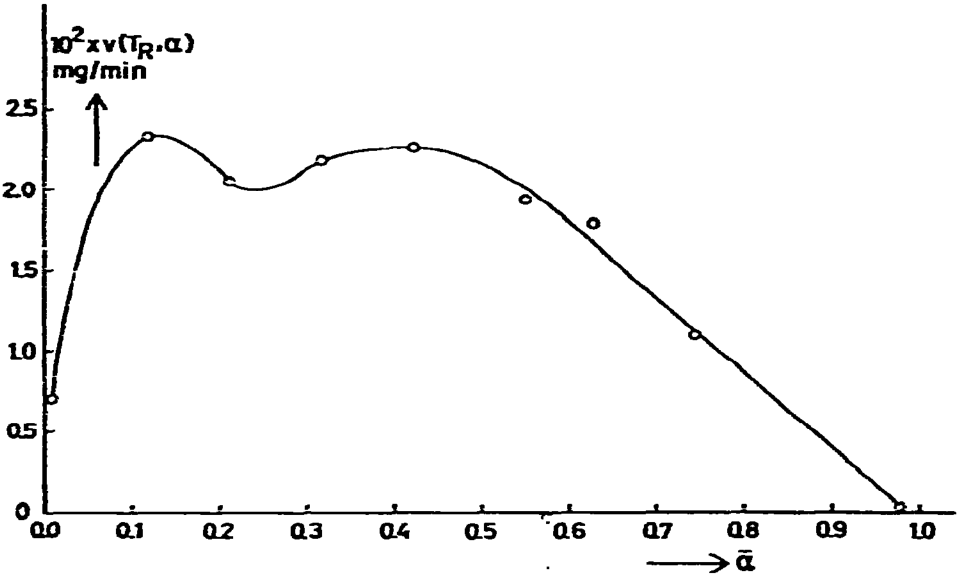

Fig. 2. The decomposition rate $v(T_R, \alpha)$ of single crystal I of K_2PdCl_4 at a reference temperature of 128.9°C, plotted against the degree of decomposition $\bar{\alpha}$. For the individual crystals, the shape of the curves varies more or less.

temperature[5]. From the slopes of the steps in the weight change curve, representing the rates of decomposition, the following formulae can be derived:

$$v = -\frac{dG}{dt} = k \cdot A \tag{1}$$

$$v(T_R, \alpha) = k(T_R) \cdot A(T_R, \alpha) \tag{2}$$

$$v(T_i, \alpha) = k(T_i) \cdot A(T_i, \alpha) \tag{3}$$

where the following symbols are used: v, rate of decomposition of the specific step; k, rate constant at the specific temperature; A, extent of the reaction interface at the specific step; $\alpha = (G_0 - G_t)/(G_0 - G_\infty)$, degree of progress of the reaction; G_0, weight at $t = 0$; G_t, weight at $t = t$; G_∞, weight after completion of the reaction; T_R, reference temperature; and T_i, temperature of a specific step.

When $v(T_R, \alpha)$ is plotted against the mean value of the degree of decomposition α of a step, a rather smooth curve is obtained (see Fig. 2, which applies to single crystal I). This supports the assumption that discontinuities, which might appear in the development of the interface, can be neglected. With each mean α value of a step, carried out at one specific temperature T_i, there corresponds a value of $A(T_i, \alpha)$, which must lie between the $A(T_R, \alpha)$ values belonging to the adjacent points on the $v(T_R, \alpha)$ versus $\bar{\alpha}$ curve, obtained at the reference temperature. Therefore, the value of $v(T_R, \alpha)$ which should correspond to this value of the interface $A(T_i, \alpha)$, and thus to the mean α value of the step at the temperature T_i, can be approximated by interpolation between the points of Fig. 2.

TABLE 1

STEPWISE DECOMPOSITION OF SINGLE CRYSTAL I OF K_2PdCl_4. THE REFERENCE TEMPERATURE T_R IS 128.9 °C; $v(T_i, a)$ IS THE DECOMPOSITION RATE AT TEMPERATURE T_i AND AT THE MEAN DEGREE OF DECOMPOSITION $\bar{a}$

T_i(°C)	$v(T_i, a)$ (mg min^{-1})	$\bar{a}$[a]	$v(T_R, a)$ (mg min^{-1})	$v(T_i, a)/v(T_R, a)$
110.7	$1.02 \cdot 10^{-2}$	0.38	$2.27 \cdot 10^{-2}$	0.449
113.6	$0.90 \cdot 10^{-2}$	0.59	$1.86 \cdot 10^{-2}$	0.484
113.8	$1.19 \cdot 10^{-2}$	0.37	$2.26 \cdot 10^{-2}$	0.527
117.1	$1.15 \cdot 10^{-2}$	0.58	$1.90 \cdot 10^{-2}$	0.605
118.0	$1.32 \cdot 10^{-2}$	0.36	$2.25 \cdot 10^{-2}$	0.587
121.2	$1.40 \cdot 10^{-2}$	0.18	$2.20 \cdot 10^{-2}$	0.636
124.6	$1.85 \cdot 10^{-2}$	0.34	$2.23 \cdot 10^{-2}$	0.830
125.2	$1.65 \cdot 10^{-2}$	0.57	$1.98 \cdot 10^{-2}$	0.833
125.4	$1.78 \cdot 10^{-2}$	0.17	$2.26 \cdot 10^{-2}$	0.788
130.5	$2.50 \cdot 10^{-2}$	0.14	$2.32 \cdot 10^{-2}$	1.078
130.9	$1.52 \cdot 10^{-2}$	0.73	$1.24 \cdot 10^{-2}$	1.226
132.7	$2.43 \cdot 10^{-2}$	0.24	$2.01 \cdot 10^{-2}$	1.209
133.1	$2.00 \cdot 10^{-2}$	0.66	$1.53 \cdot 10^{-2}$	1.307
137.8	$3.09 \cdot 10^{-2}$	0.06	$1.92 \cdot 10^{-2}$	1.609
138.6	$3.35 \cdot 10^{-2}$	0.47	$2.23 \cdot 10^{-2}$	1.502
140.3	$3.87 \cdot 10^{-2}$	0.51	$2.16 \cdot 10^{-2}$	1.792
140.8	$2.65 \cdot 10^{-2}$	0.69	$1.39 \cdot 10^{-2}$	1.906

[a] The sequence of the steps during the decomposition follows from the increasing value of $\bar{a}$.

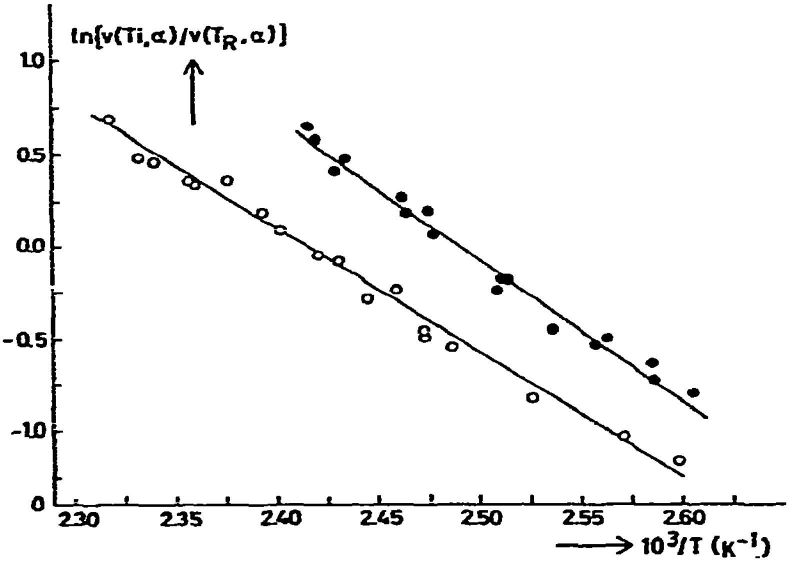

Fig. 3. Arrhenius plot of single crystal I(●) and powder I(○) of K_2PdCl_4.

This value of $\nu(T_R, \alpha)$ can be expressed as

$$\nu(T_R, \alpha) = k(T_R) \cdot A(T_i, \alpha) \tag{4}$$

In this way, the activation energy E_A, given by the Arrhenius equation

$$k = k_0 \exp(-E_A/RT) \tag{5}$$

can be obtained for each temperature T_i by division of the expressions (3) and (4). This gives (see Table 1)

$$\ln \{\nu(T_i, \alpha)/\nu(T_R, \alpha)\} = -(1/T_i - 1/T_R) \cdot E_A/R \tag{6}$$

The Arrhenius plot of the logarithmic term of eqn. (6) vs. $1/T_i$ yields a straight line. This indicates that the assumed mechanism is a valid one.

The value of E_A, obtained from the Arrhenius plot is (see Fig. 3), for single crystal I, 15.1 ± 0.4 kcal mol^{-1}. The mean value of E_A, for all three decomposed single crystals, is 15.2 ± 0.5 kcal mol^{-1}.

DECOMPOSITION OF POWDERS OF K_2PdCl_4

The results of isothermally-decomposed powders could not be fitted to one of the well-known kinetic laws, which are based on models concerning nucleation and growth in heterogeneous systems[8, 9]. Therefore, the stepwise decomposition method

TABLE 2

STEPWISE DECOMPOSITION OF POWDER I OF K_2PdCl_4. THE REFERENCE TEMPERATURE T_R IS 139.7°C; $\nu(T_i, a)$ IS THE DECOMPOSITION RATE AT TEMPERATURE T_i AND AT THE MEAN DEGREE OF DECOMPOSITION $\bar{a}$

T_i (°C)	$\nu(T_i, a)$ (mg min^{-1})	$\bar{a}$[a]	$\nu(T_R, a)$ (mg min^{-1})	$\nu(T_i, a)/\nu(T_R, a)$
111.7	$2.00 \cdot 10^{-2}$	0.01	$6.42 \cdot 10^{-2}$	0.312
115.8	$2.50 \cdot 10^{-2}$	0.02	$7.04 \cdot 10^{-2}$	0.355
122.7	$3.33 \cdot 10^{-2}$	0.03	$7.64 \cdot 10^{-2}$	0.436
129.1	$3.25 \cdot 10^{-2}$	0.52	$5.65 \cdot 10^{-2}$	0.575
131.3	$5.25 \cdot 10^{-2}$	0.04	$8.33 \cdot 10^{-2}$	0.630
131.3	$3.33 \cdot 10^{-2}$	0.53	$5.47 \cdot 10^{-2}$	0.609
133.5	$4.67 \cdot 10^{-2}$	0.51	$5.91 \cdot 10^{-2}$	0.790
135.8	$7.18 \cdot 10^{-2}$	0.33	$9.55 \cdot 10^{-2}$	0.752
138.2	$8.50 \cdot 10^{-2}$	0.35	$9.26 \cdot 10^{-2}$	0.918
139.9	$1.83 \cdot 10^{-2}$	0.65	$1.93 \cdot 10^{-2}$	0.948
143.2	$9.33 \cdot 10^{-2}$	0.40	$8.53 \cdot 10^{-2}$	1.094
144.7	$12.67 \cdot 10^{-2}$	0.22	$10.50 \cdot 10^{-2}$	1.207
147.7	$15.25 \cdot 10^{-2}$	0.12	$10.14 \cdot 10^{-2}$	1.504
150.6	$14.50 \cdot 10^{-2}$	0.26	$10.32 \cdot 10^{-2}$	1.405
151.2	$11.33 \cdot 10^{-2}$	0.43	$7.93 \cdot 10^{-2}$	1.429
154.2	$11.67 \cdot 10^{-2}$	0.45	$7.38 \cdot 10^{-2}$	1.581
155.6	$6.63 \cdot 10^{-2}$	0.58	$4.10 \cdot 10^{-2}$	1.617
158.3	$7.17 \cdot 10^{-2}$	0.60	$3.59 \cdot 10^{-2}$	1.997

[a] The sequence of the steps during the decomposition follows from the increasing value of $\bar{a}$.

outlined above was also applied to the powders. The reaction rates of two different powders were plotted for the same reference temperature as a function of the degree of decomposition. This confirmed the idea that, as for single crystals, different samples do not behave reproducibly, due to the irregularities of the reaction interface. The calculations were based on the same equations used for the single crystals. The results for one powder are listed in Table 2 and illustrated in Figs. 3 and 4. The value of the activation energy for this powder is, (powder I), $E_A = 13.4 \pm 0.4$ kcal mol^{-1}. The mean value of the activation energy for both decomposed powders is $E_A = 13.5 \pm 0.4$ kcal mol^{-1}.

These values are smaller than those obtained for single crystals. This can be explained from the fact that the influence of the nucleation in the combined decomposition process is larger for powders than for single crystals, owing to the small dimensions of the powder particles[5]. Since the nucleation reaction probably has a lower activation energy than the growth, this results in a lower overall activation energy for the decomposition of the powders. Microscopic observations revealed that even at rather low decomposition temperatures all powder particles are covered within a few minutes with a black layer of decomposed material. This supports the assumption that the nucleation rate is fast.

CONCLUSIONS FOR K_2PdCl_4

(i). The decomposition rate is determined by a combined process of nucleation and growth for single crystals as well as for powders.

(ii). The decomposition rate of the single crystals and of the powders is proportional to the extent of the irregular interface.

(iii). Only the activation energy of the combined process of nucleation and growth can be calculated.

COMPARISON OF THE RESULTS OBTAINED FOR K_2PtCl_4, K_2PdCl_4, Rb_2PdCl_4 AND K_2PdBr_4

(1). The decomposition rate of the single crystals of K_2PtCl_4 is only determined by growth, whereas for K_2PdCl_4 both nucleation and growth are involved.

(2). Cross-sections of partly-decomposed single crystals of K_2PtCl_4 reveal that the reaction interface is smooth and that the thickness of the decomposed layer is equal in all crystallographic directions. In the case of K_2PdCl_4 and Rb_2PdCl_4 the reaction interface is very irregular and consists mainly of sheets perpendicular to the C-axis. For K_2PdBr_4 the interface resembles that of K_2PtCl_4; however it is less flat (see Fig. 1). These differences are probably due to lattice defects. Microscopic observations of the single crystals reveal that K_2PdCl_4 and Rb_2PdCl_4 develop many lattice defects, lying along (001) planes. At the {100} crystal surfaces these lattice defects show as cracks perpendicular to the C-axis. The K_2PdBr_4 crystals are more perfect, while the K_2PtCl_4 crystals are the most perfect ones. SEM views of K_2PtCl_4 and K_2PdCl_4 crystals confirm these observations.

(3). The decomposition of powders of K_2PtCl_4 is controlled by nucleation, while for K_2PdCl_4 the decomposition rate is governed by both nucleation and growth. Microscopic observations of the decomposition process of Rb_2PdCl_4 and K_2PdBr_4 powders reveal the same behaviour as for K_2PdCl_4.

(4). In the case of K_2PtCl_4, the activation energies for growth, E_G, and nucleation, E_N, are 30.8 ± 1.0 and 16.2 ± 1.4 kcal mol^{-1}, respectively, while the activation energy of K_2PdCl_4 varies from 15.3 ± 0.5 kcal mol^{-1} for single crystals to 13.5 ± 0.4 kcal mol^{-1} for powders.

(5). It follows from conclusions (3) and (4) that nucleation occurs more easily for the three palladium salts than for K_2PtCl_4. Although, unfortunately, the activation energies required for the nucleation of the Pd salts cannot be determined separately, these energies are probably lower than for K_2PtCl_4.

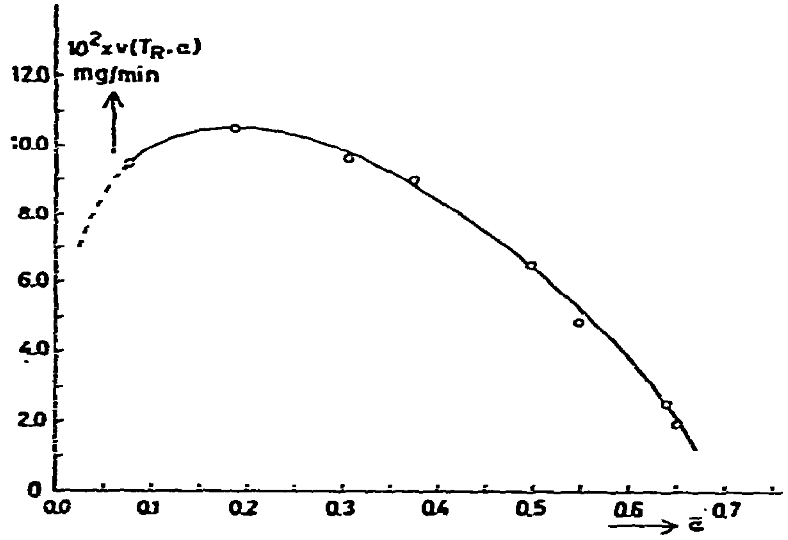

Fig. 4. The decomposition rate $r(T_R, a)$ of powder I of K_2PdCl_4 at a reference temperature of 139.7 °C, plotted against the degree of decomposition $\bar{a}$. For the individual powders, the shape of the curves varies more or less.

(6). When the orientation relationships between the single crystals of all four compounds and their decomposition products are compared, it is noticed that for the Pd salts only two relationships are found, as against four in the case of K_2PtCl_4. The orientations of the new phases are probably settled during the nucleation process. Less orientation relationships can follow from a lower value of the activation energy required for nucleation, since it may be assumed that a lower activation energy permits fewer orientations to develop. Finally, it is concluded that the orientation relationships shown by the different crystals can be related to differences and resemblances in their kinetic behaviour when geometrical factors are excluded.

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REFERENCES

1 G. M. van Rosmalen and W. G. Burgers, *Proc. K. Ned. Akad. Wet. Ser. B*, 77 (1974) 376.
2 K. R. Lawless and A. T. Gwathmey, *Acta Metall.*, 4 (1956) 153.
3 H. G. Schneider and V. Ruth, *Advances in Epitaxy and Endotaxy: Physical Problems of Epitaxy*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1971.
4 H. G. Schneider and V. Ruth, *Advances in Epitaxy and Endotaxy: Selected Chemical Problems*, Akadémiai Kiadó, Budapest, 1976.
5 W. G. J. Marchée, G. Hakvoort and G. M. van Rosmalen, *Thermochim. Acta*, 13 (1975) 321.
6 W. G. J. Marchée and G. M. van Rosmalen, *J. Cryst. Growth*, 39 (1977) 358.
7 J. C. van Dam, G. Hakvoort, J. C. Jansen and J. Reedijk, *J. Inorg. Nucl. Chem.*, 37 (1975) 713.
8 J. Sestâk, *Thermal Analysis, Proc. 3rd ICTA Davos*, Vol. 2, 1971, p. 3.
9 S. F. Hulbert, *J. Br. Ceram. Soc.*, 7 (1970) 11.