Aspects of the Thermal Decomposition of ε-Zinc Hydroxide: A Kinetic Compensation Effect †

By **Giulio G. T. Guarini,*** Institute of Physical Chemistry, The University of Florence, Via Gino Capponi 9, 50121 Firenze, Italy
Roberto Spinicci, Institute of Applied Chemistry, The University of Florence, Via S. Marta 3, 50139 Firenze, Italy

Differential scanning calorimetry and quantitative thermal analysis of the kinetics of thermal decomposition of zinc and related hydroxides, undertaken in order to investigate the relations between the decomposition kinetics and the catalytic properties of the resulting oxides, has revealed the existence of a remarkable compensation effect for ε-$Zn(OH)_2$. Optical microscopy has been used as a complementary technique to study the formation and growth of product nuclei during the thermal decompositions and to test the reliability of the thermal methods. The microscopic study, by the etching technique, of the points of emergence of the dislocations, reveals the existence of two distinct types of line defects, one of which is more conducive for the reaction. The results are interpreted in terms of a Sosnovsky-type mechanism, and the elastic strain energy of the dislocations is considered to be the main contributor to the lowering of the activation energy of the nucleation process.

DESPITE the criticisms raised[1] about the applicability of the Arrhenius equation to the reactions involved in the thermal decomposition of solids, an attempt has been made to give an experimental explanation of a particularly evident compensation effect found in a study, by thermal methods, of the kinetics of thermal decomposition of ε-$Zn(OH)_2$. This compound has been the subject of previous studies in these laboratories[2] in view of a possible correlation between the catalytic activity of zinc oxides, obtained on decomposition of a number of parent compounds, and the corresponding kinetics of decomposition. The physical meaning of the compensation effect is not yet completely understood and, while some workers ascribe it to the influence of physicochemical factors on the course of the reaction, others invoke the inadequacy of the Arrhenius equation itself when applied to heterogeneous reactions in general.[3] Our aim was therefore to ascertain the validity of one or other of these hypotheses.

We support the results obtained by differential scanning calorimetry (d.s.c.) and quantitative thermal analysis with those obtained by optical microscopy. In this way it is possible to get more detailed information, useful for a better understanding of the calorimetric results and of some of their discrepancies. The results reported refer to the initial portion of the reaction: optical microscopy cannot be used beyond the complete coverage of the surface by decomposition nuclei. For this portion of the reaction previous studies[2] have already shown that an $n = 2$ power law[4,5] is applicable. To gain more information about the formation and growth of product nuclei, the points of emergence of line defects on the surface of single crystals were revealed by the etching technique. It is well

---

† Presented at the 5th I.C.T.A. Kyoto, Japan, 1st—6th August, 1977.

[1] P. D. Garn, *Crit. Rev. Analyt. Chem.*, 1972, **3**, 65.

[2] G. G. T. Guarini, R. Spinicci, and D. Donati, *Proc. 25th Internat. Meeting of the Société de Chimie Physique de France*, Dijon, 8—12th July, 1974, Elsevier, Amsterdam, 1976, pp. 295—301.

[3] A. K. Galwey, *Adv. Catalysis*, 1977, **26**, 247.

[4] P. W. M. Jacobs and F. C. Tompkins, 'Chemistry of the Solid State,' ed. W. E. Garner, Butterworths, Oxford, 1955.

[5] D. A. Young, 'Decomposition of Solids,' Pergamon, Oxford, 1966.

known[6] that dislocations may play a fundamental role in nucleation of heterogeneous reactions involving solids.

EXPERIMENTAL

Microcrystalline powders and small (up to *ca.* 0.7 mm) single crystals of ε-$Zn(OH)_2$ were prepared by slight modifications of the method suggested by Secco.[7] *X*-Ray analysis as well as the morphology agreed perfectly with the corresponding data in the literature.[8]

Thermal curves were obtained using a Perkin-Elmer DSC-1b differential scanning calorimeter and a Mettler TA 2000 differential thermal analyser, both at constant and at linearly increasing temperature. A stream of dry nitrogen at *ca.* 20 ml min^{-1} was preferentially used (even if there was no dependence of the kinetic parameters on the N_2 flow) in order to avoid any kind of retention of the water formed during the decomposition, particularly by the thin layer of graphite which was spread on the sample. The use of this layer, spread on the reference pan also, is designed to balance the thermal emissivity[9] thus stabilizing the baseline.

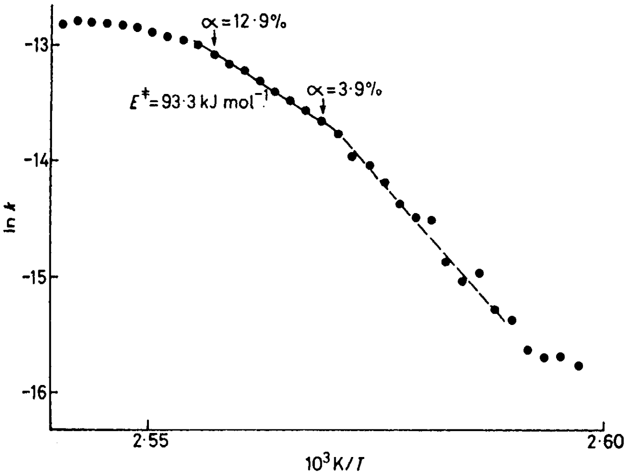


FIGURE 1 Typical Arrhenius plot of the initial portion of the reaction constructed from a calorimetric run at variable temperature

At the end of each run the product of the decomposition was accurately weighed and the amount of water lost was determined. The latter is between 85 and 90% of the theoretical value depending on the scan speed used in the variable-temperature runs and on the value of the temperature in the constant-temperature experiments. In some of the former experiments the sample was allowed to reach temperatures *ca.* 100 K higher than that corresponding to the end of the reaction: in these cases the water loss was stoicheiometric. We therefore conclude that the reaction is complete at the end of the corresponding thermal curve, a residual amount of water being adsorbed on the ZnO produced.

A Reichert Zetopan microscope, equipped with an interferometer and interference contrast as well as a hot stage, was used to study the formation and growth of nuclei until the examined crystal surface was completely covered with the product. Since the temperature of the hot stage was only adjustable and not programmable, only constant-temperature runs were performed: the results with or without a nitrogen stream were identical.

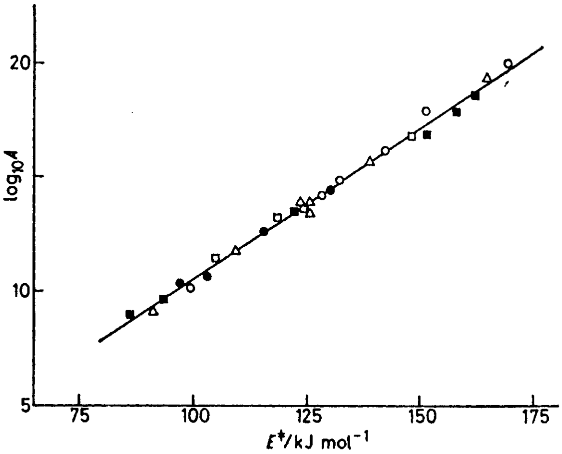


FIGURE 2 Compensation-effect plot ($\log_{10}A$ against $E^{\ddagger}$) for the second range of applicability of the $n = 2$ power law (0.06—0.10 $< \alpha <$ 0.16—0.20). Scan speed = 4 (□), 2 (■), 1 (○), and 0.5 K min^{-1} (△). (●), At constant temperature

The orthorhombic ε-$Zn(OH)_2$ crystals were etched by immersing them in a 1 mol dm^{-3} $[NH_4]Cl$ solution for *ca.* 1 min at room temperature (*ca.* 293 K). Subsequently, the crystals were rinsed in distilled water and dried with soft filter paper.

RESULTS AND DISCUSSION

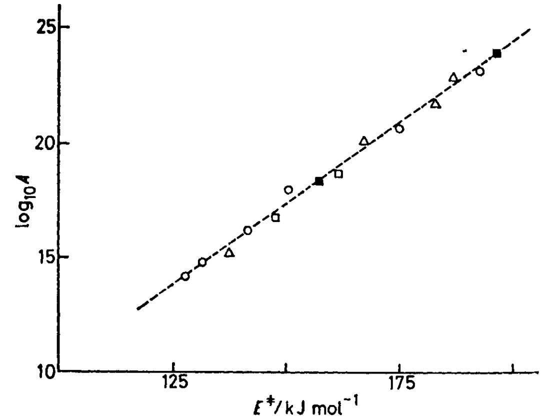


FIGURE 3 Compensation-effect plot for the first range of applicability of the $n = 2$ power law at the onset of the decomposition (0.01 $< \alpha <$ 0.04—0.05). Details as in Figure 2

Remembering that the samples used were crystalline powders from different preparative sources with differences in the degree of ageing, the Arrhenius plots constructed from the calorimetric runs at variable temperature showed (with some uncertainty) a range of fractional decomposition from $\alpha = 0.06$—0.10 to $\alpha =$ 0.16—0.20 in which an $n = 2$ power law is applicable (Figure 1). The corresponding values of the activation energy were 84.4—165.5 kJ mol^{-1}, and the values of the

---

[6] J. M. Thomas, *Adv. Catalysis*, 1969, **18**, 293.

[7] O. K. Srivastava and E. A. Secco, *Canad. J. Chem.*, 1967, **45**, 579, 585.

[8] R. B. Corey and R. G. Wyckoff, *Z. Krist.*, 1933, **86**, 8.

[9] G. G. T. Guarini, R. Spinicci, and D. Donati, *J. Therm. Analysis*, 1974, **6**, 405.

logarithm of the pre-exponential factor ($\log_{10}A$) varied between 8.5 and 18.4. A plot of the values of $\log_{10}A$ against $E^{\ddagger}$ gave a straight line, underlying the existence of a compensation effect (Figure 2).

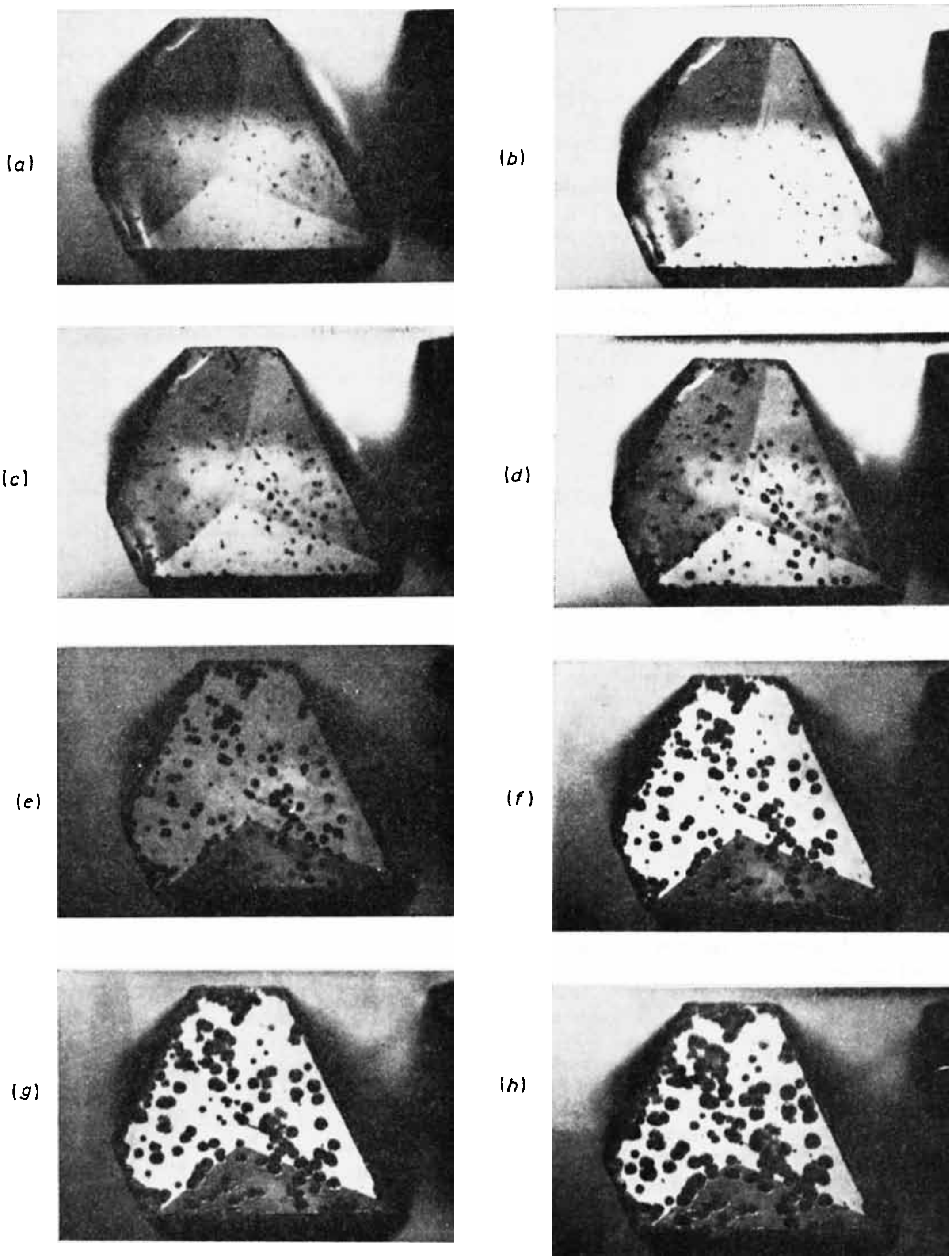


FIGURE 4 Sequence of photomicrographs recorded at increasing time [120 (*a*), 180 (*b*), 260 (*c*), 360 (*d*), 450 (*e*), 555 (*f*), 657 (*g*), and 795s (*h*)] during the thermal decomposition of a {110} face of a ε-$Zn(OH)_2$ single crystal at 385 K. Magnification, times 270

In a number of runs, particularly those at low scan speed, the $n = 2$ power law is also followed for a short period at the onset of the decomposition ($0.01 < \alpha <$ 0.04—0.05). In this case the activation energies and pre-exponential factors were higher than those related to the above period: $E^{\ddagger} = 125.6$—201.9 kJ mol^{-1} and $\log_{10}A = 14.2$—24; the linear relation between these values and the consequent compensation effect is shown in Figure 3.

A series of thermal experiments was also performed at a number of constant temperatures in the range 375—391 K, each series referring to samples from different preparations or different ageings. The analysis of the thermal curves and the Arrhenius plots confirmed the applicability of the $n = 2$ power law to the initial portion of the reaction ($0.03 < \alpha < 0.22$), with activation energies ranging from 98.8 to 135.2 kJ mol^{-1} and $\log_{10}A$ ranging from 9.1 to 14.5. (Unfortunately it was not possible to confirm that an $n = 2$ power law is also applicable to the onset of the decomposition because of the time required for stabilization of the baseline after introducing the sample into the pan at the fixed temperature.) These values also fall on the same straight line obtained for the second period of validity of the $n = 2$ power law from variable-temperature runs (Figure 2).

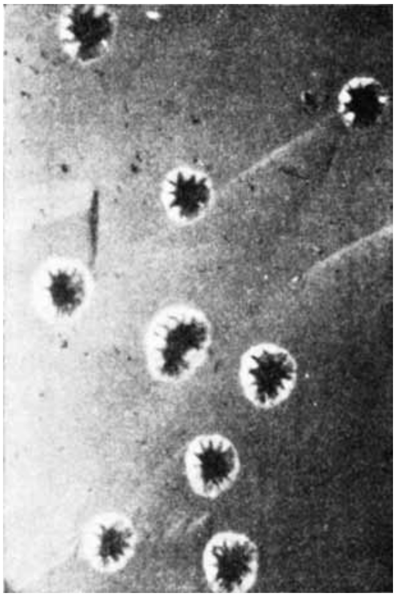


FIGURE 5 Shape of the nuclei on the ε-Zn(OH)$_2$ surfaces. Magnification 1 300 times

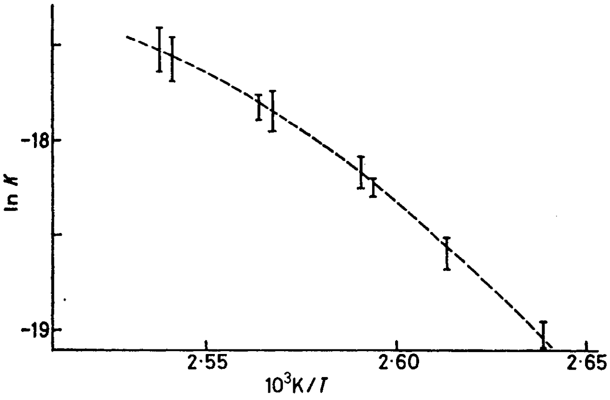


FIGURE 6 Plot of ln k against $1/T$ obtained from thermal decompositions on the hot stage of the microscope for the {110} faces. The ranges correspond to the values of the rate constants determined at a particular temperature by measuring the diameter of a number of nuclei on the {110} faces of several crystals

According to the analysis by Bond,[10] from the compensation-effect plots, values of 381.6 and 390.2 K were deduced for the isokinetic temperature, T_i, of the first and of the subsequent range of applicability of the $n = 2$ power law. The exact meaning of the isokinetic temperature is not completely understood: however, for the present decomposition there is strong experimental evidence that non-isothermal runs, performed at such a scan speed as to allow the isokinetic temperature to fall within the corresponding range of validity of the power law, are the ones giving the most conflicting results.

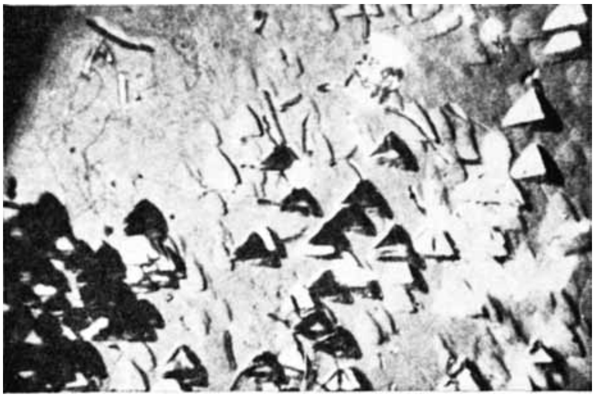


FIGURE 7 Shape of the etch pits on a {011} face. It is possible to recognize dark (deeper) and light (flatter) pits. Magnification, 640 times

The existence of the spread of values for the activation energy prompted us to use optical microscopy in order to gain deeper insight into the nucleation and growth processes. The two main faces ({110} and {011}, respectively trapezoidal and triangular in shape) of the orthorhombic crystals of ε-Zn(OH)$_2$ were studied. The sequence of photomicrographs in Figure 4, recorded during one of many runs at constant temperature, shows that: (*i*) the nucleation is random; (*ii*) after a certain induction period the nuclei appear quickly and, in the runs at the highest temperatures, almost contemporaneously; and (*iii*) the nuclei are almost circular on both faces (see also Figure 5).

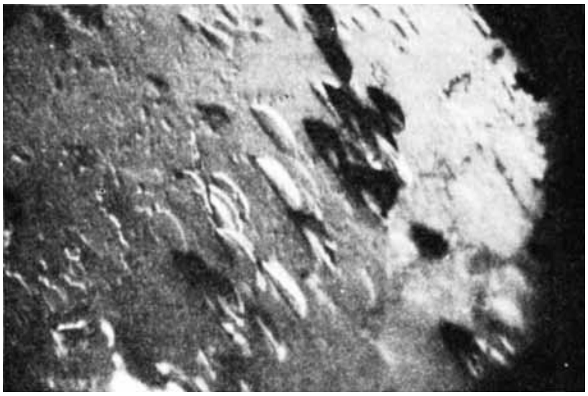


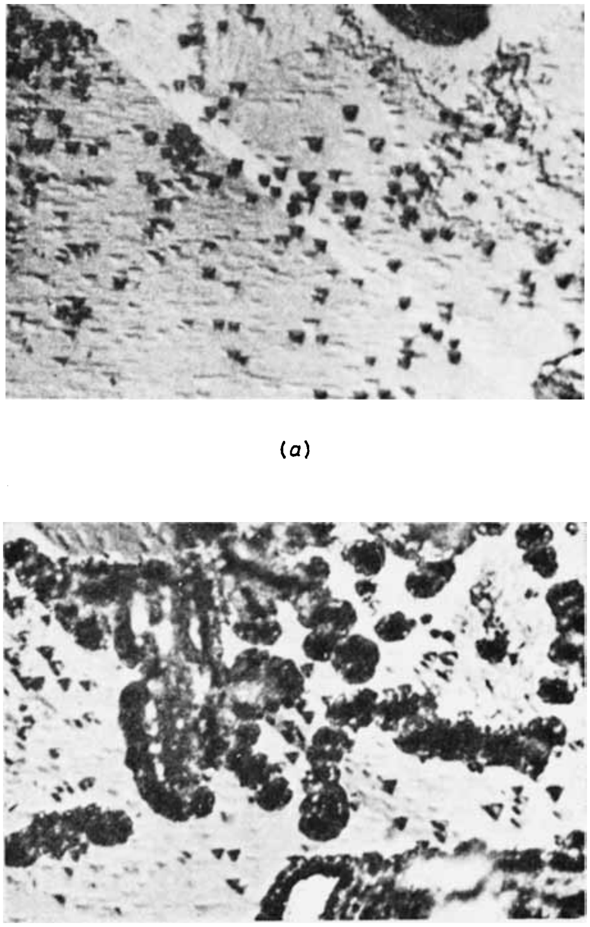
FIGURE 8 Shape of the etch pits on a {110} face. Details as in Figure 7

The features of this nucleation process therefore did not allow (in the useful range of temperature) reliable determination of the rate of nucleation and of the

---

[10] G. C. Bond, 'Catalysis by Metals,' Academic Press, New York, 1972.

corresponding kinetic parameters; instead it was possible to determine the rate of radial growth of the nuclei until the surface was almost completely covered with the product. One of the corresponding Arrhenius plots is reported in Figure 6. This and other such plots are not rectilinear, and the curves are slightly different both between the two faces studied and between corresponding faces of crystals taken from different batches. From the tangents to the curves at the points of minimum and maximum gradient (higher and lower temperatures), values of 77.2 and 165.5 kJ mol^{-1} were deduced for the activation energies.


(*a*)

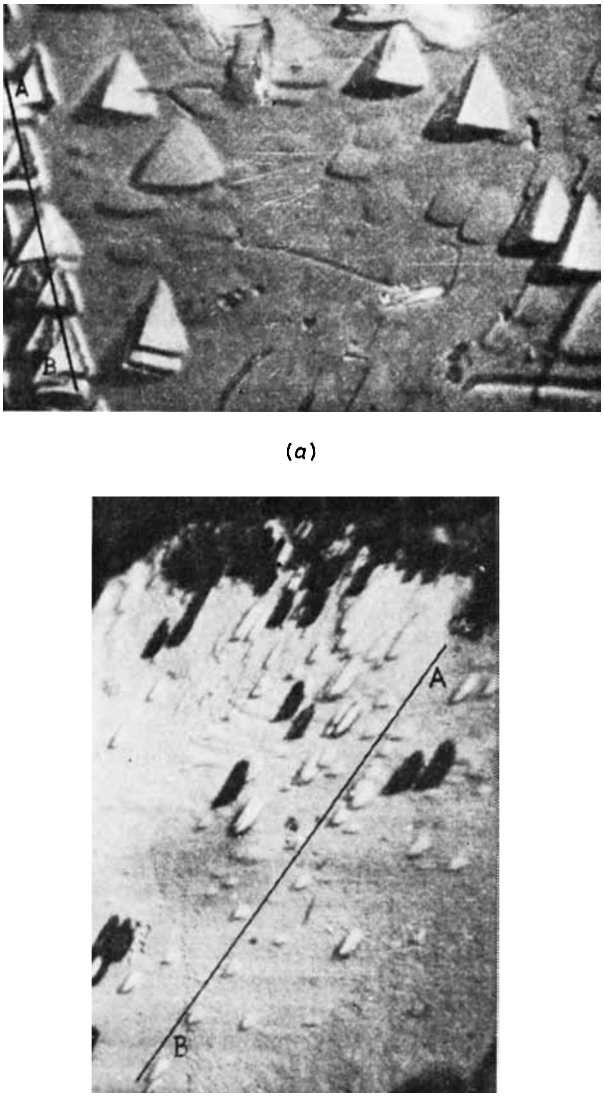
(*b*)

FIGURE 9 Etching (*a*) and subsequent partial decomposition (*b*) of {011} face of ε-Zn(OH)$_2$. The imperfect 1 : 1 correspondence in this and other experiments is mainly due to some small scratches on the surface and to slight mechanical stresses produced by the repeated handling of the crystals for etching and decomposition. Magnification, 480 times

It clearly emerges that, at the highest temperatures of our investigation, the rate of radial growth on the surfaces is lower than expected. On the other hand, we found, by weighing, that the decomposition had already advanced beyond 35% when the nuclei had almost completely covered the observed surface: this unusually high value of the fractional decomposition suggested that two main mechanisms for the growth were concurrent rather than sequential: (*a*) a two-dimensional mechanism as revealed by optical microscopy, having a higher activation energy and prevailing at the lowest temperatures; (*b*) a one-dimensional mechanism, directed towards the inner part of the crystal, with a lower activation energy and prevailing at the highest temperatures.

Some independent evidence was necessary at this stage to collate the experimental results: for example, there may be different kinds of active defects which hold the key to understanding the whole process.

Etch studies of the two main faces of ε-Zn(OH)$_2$ crystals were therefore undertaken; photomicrographs of the etched surfaces are shown in Figures 7 and 8.



(*a*)

(*b*)

FIGURE 10 Comparison of the sizes of aligned (A—B) and isolated etch pits: (*a*) {011} face; (*b*) {110} face. Magnification, 720 and 450 times respectively

As expected, the etch pits differed in shape, being triangular and trapezoidal on {011} and {110} respectively. The most interesting feature was that on the same surface there were two kinds of etch pits, namely dark (deeper) and light (flatter). (Only rarely has a feature of this kind been previously reported: see Livingston [11] who interpreted the effect as being due to the possibility of the etchant distinguishing positive and negative edge dislocations.) Decomposition runs conducted with previously etched crystals showed that dehydration nuclei formed almost exclusively on the dark pits or in their nearest surroundings (Figure 9): therefore, of the two types of defects, only one appeared to be active for the decomposition. Conversely, the etching of partially decomposed crystals showed that it was almost impossible to obtain etch pits on already nucleated crystal surfaces unless the decomposition was stopped when the nuclei were so small as to be detectable only by using the highest magnification ($>\sim$1 000 times).

This means that the dislocations, becoming mobile at increasing temperature and being, in all probability, of a similar kind (because of the constancy of size of the dark and light pits in Figure 7) but of opposite sense or sign, tend to annihilate one another. Therefore, at the lowest temperatures the dislocations are rather crowded and strongly interact, while at the highest temperatures the annihilation mechanism becomes effective, leaving fewer dislocations which are isolated and non-interacting.

Since nuclei are usually better formed at the emergence points of dislocations, the process of nucleation is probably strongly conditioned by the dislocation interactions. In other words, the experimental results indicate that the non-interacting dislocations isolated at higher temperatures contribute to a lowering of the activation energy of the nucleation process much more than the crowded, strongly interacting, low-temperature dislocations. In fact, the nucleation process has a lower activation energy at higher temperatures (and the nuclei appear very quickly and almost contemporaneously).

This means that, at least for ε-Zn(OH)$_2$ crystals, the elastic strain energy is more important for the reactivity than the core energy; [12] the experimental evidence that alignments of etch pits are seldom observed and that, when observed (Figure 10), the aligned etch pits are often smaller than the corresponding isolated ones, may be considered an indirect confirmation of the above statement.[12] On the other hand, the structure of the core of the dislocation must be of crucial importance as shown by the preferential nucleation on dark (deeper) etch pits.

We think therefore that the first $n = 2$ power-law range, at the lowest temperatures, refers to a relatively slow nucleation followed by the more activated mechanism of growth (surface growth), while the second $n = 2$ power-law range, at higher temperatures, corresponds to a quick (strain-energy assisted) nucleation followed by the less activated mechanism of growth (progress of the reaction along the dislocation line). The interpretation given for the spread of activation energies and pre-exponential factors found in different experiments is therefore strictly similar to the one given by Sosnovsky [13] for the compensation effect in catalytic reactions; the spread of values found is explained as the outcome of the dislocation density, their interactions and their annihilation mechanism.

On the basis of this interpretation we observe that, when describing the decomposition of solids in terms of the Arrhenius equation, the values of the activation energy and pre-exponential factor must be considered to result from the different reactant states and different activated complex states, according to the lattice distortions near or far from the dislocations, and according to the phenomena involved in the progress of the reactant–product interface on the surface or towards the inner part of the crystals.

Conclusions.—The existence of a compensation effect as shown by thermal studies of the decomposition of ε-Zn(OH)$_2$ may be explained by a Sosnovsky-type mechanism. This conclusion could not have been made without the auxiliary use of optical microscopy. At the same time, the latter technique has shown the reliability of thermal methods in recording the thermal events of the samples. Indeed, the present work shows that thermal curves contain the full information, the only problem being in its correct interpretation. This can seldom be achieved without any independent sources of information. In the present instance both the nucleation and etching studies were crucial. However, a deeper insight into the detailed mechanism of the thermal decomposition of crystalline ε-Zn(OH)$_2$ will be gained only when studies, now in progress, to determine more information relating to dislocations (*e.g.* an assessment of the slip planes and directions of dislocations) are completed.

We thank Consiglio Nazionale delle Ricerche (Rome) for support.

[7/2273 *Received, 28th December*, 1977]

---

[11] J. D. Livingston, 'Direct Observation of Imperfections in Crystals,' eds. G. B. Newkirk and J. H. Wernick, Wiley, New York, 1962, p. 115.

[12] For a discussion see J. M. Thomas, E. L. Evans, and T. A. Clarke, *J. Chem. Soc.* (*A*), 1971, 2338 and refs. therein.

[13] H. M. C. Sosnovsky, *J. Phys. and Chem. Solids*, 1959, **10**, 304.