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About SnF_2 Stannous Fluoride
IV. Kinetics of the $\alpha \rightarrow \gamma$ and $\beta, \gamma \rightarrow \alpha$ Transitions

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The kinetics of the reconstructive first order phase transitions $\alpha \rightarrow \gamma$ (upon heating) and $\beta, \gamma \rightarrow \alpha$ (upon cooling) of SnF_2 were studied by quantitative X-ray powder diffraction. The main feature of the kinetics is that these transformations are incomplete over a wide temperature range. Consequently it is not possible to fit the experimental data using the usual solid state rate expressions. Although these transitions are not reversible (large hysteresis) the empirical use of a kinetic model of a reversible transformation provides a good fit. The $\alpha \rightarrow \gamma$ transformation was also investigated by D.T.A.; this transition was found to be greatly influenced by particle size: the transition temperature increases with grain size, and its enthalpy decreases. The X-ray investigation revealed that the process of the $\alpha \rightarrow \gamma$ transformation involves an intermediate noncrystalline phase named the "transition phase." It is suggested that the transition proceeds through a process of fragmentation-reconstruction.

Introduction

Elucidation of the mechanisms of structure changes in solids requires detailed studies of nucleation and growth rates as well as of crystallographic relationships. The kinetics of transformation of several inorganic materials have been previously investigated (e.g., in TiO_2, SiO_2, $AgNO_3$). Various kinetic equations can be used to fit the experimental data; most of them are based on the following three models (*1*): acceleratory α-time curves (power laws), sigmoid α-time curves (Avrami–Erofeev, Prout–Tompkins), deceleratory α-time curves (geometrical models, diffusion mechanisms, use of "order of reaction"). However, two recent publications (*2, 3*) assumed that the notion of "velocity of transition" is inapplicable and that it is hardly possible to discover a mechanism of phase transitions by way of kinetic investigation only.

Tin difluoride SnF_2 exists in three polymorphic forms (*4*): α(monoclinic), β(orthorhombic), γ(tetragonal). Their crystal structures were recently elucidated (*5–7*): α-SnF_2 exhibits a molecular structure (presence of Sn_4F_8 tetramers); β- and γ-SnF_2 are related to the rutile and the cristobalite types. The stereoactivity of the lone pair of Sn(II) is apparent in all three phases. The α modification is the stable form at room temperature. Upon heating, it transforms to γ-SnF_2 which is stable up to the melting point (215°C) and can be kept metastable down to 66°C. The β phase is a distorted form of γ and is always metasta-

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ble. The $\alpha \rightarrow \gamma$ transition is a reconstructive transformation involving changes in primary coordination $\mathscr{C} \rightarrow \mathscr{A}$ according to Brown's notation (*8*)) whereas the $\beta \rightleftarrows \gamma$ transition is displacive.

During our previous investigations of the physical properties of SnF_2 we noticed that the $\alpha \rightarrow \gamma$ transition proceeds slowly and is incomplete over a wide temperature range. In the present note, we present a study of the kinetics of this transition.

1. Experimental

The starting material, monoclinic α-SnF_2, was supplied by OSI (Omnium Scientifique et Industrielle, France).

1.1. X-ray diffraction. The ratio of α- to γ- (or β-)SnF_2 was determined by measuring the relative intensities of the X-ray diffraction peaks (area of the peaks) of the samples. Samples were 2.5-cm-diameter pellets of powdered α-SnF_2. High-temperature X-ray data were collected with a Gerard-Barret furnace (*9*) adapted to a C.G.R. (Compagnie Générale de Radiologie) powder diffractometer. All experiments were carried out under dry nitrogen; thermal stability was better than ±1°C. To ensure that the observed kinetics were not caused by a temperature gradient in the sample, the furnace was first calibrated by studying the hexagonal → orthorhombic transformation of $AgNO_3$ at 167°C (*10*). As this transformation was completed in less than 30 mn, the very long transformation times of α- to γ-SnF_2 (more than a day) or $\beta, \gamma \rightarrow \alpha$-$SnF_2$ (sometimes more than a week) cannot be attributed to a temperature gradient in the sample.

The measurements were performed at constant temperature until no transformation was observed. The amount $C(t)$ of one phase at the time t is calculated as $C(t) = I(t)/I_0$ where I_0 is the intensity of a diffraction line of this phase before transformation (for the phase which disappears) or after complete transformation (for the new phase), and $I(t)$ the intensity of the same diffraction line at time t. The intensities were measured by planimetry. It must be pointed out that, at higher temperatures, the time $t = 0$ is not well-defined because a non-negligible amount of the sample is transformed before its temperature is stabilized. The Bragg reflections used are chosen so that they are single, strong enough to allow accurate measurements, and not superposed with any of the peaks of the new phase: ($\bar{2}04$) and (224) were used for α-SnF_2, (114) and (220) for β- or γ-SnF_2. Samples of β- or γ-SnF_2 were prepared by heating pellets of α-SnF_2 for 20 mn under dry nitrogen, then cooling.

1.2. D.T.A. experiments. Only the $\alpha \rightarrow \gamma$ transition could be studied by this method. The experiments were performed either with a B.D.L. equipment (C.N.R.S.) (sample volume ~6 μl, heating rate ~600°C/hr, atmosphere = dry helium) or a Du Pont de Nemours equipment (*11*) (heating rate ~300°C/hr, atmosphere = dry nitrogen). The transition temperature was defined as the beginning of the D.T.A. peak and the area of the peak was measured by planimetry.

2. α- to γ-SnF_2 Transition

2.1. Rate Constants. Activation energy

The X-ray diffraction experiments were performed as a function of time at the following constant temperatures (°C): 142, 142.5, 143, 145, 146, 147, 148, 149, 150, 151, 153, 154, 156, 159, 160, 165, 170, and 175. The main feature of the experimental results (Fig. 1) is that, in the range 142 to 174°C, the transformation is not complete. The "limit amount" $C_\alpha(\infty)$ (residual quantity of α-SnF_2 in the sample when no further transformation is observed) is temperature dependent (Fig. 2). Below 142°C, no trans-

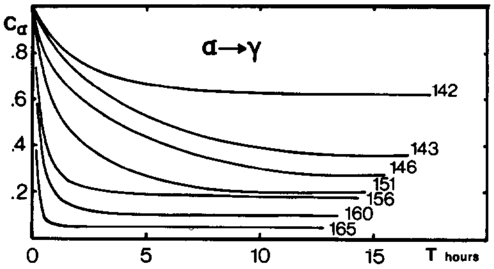

FIG. 1. α- to γ-SnF_2 transition: amount of α-SnF_2 in sample vs time at a few temperatures.

formation is observed; above 175°C it goes very rapidly to completion.

Two kinds of mathematical models are usually used to analyze the bulk kinetics of solid state transformations:

—kinetic models of irreversible homogeneous reactions (*12*); although polymorphic transitions actually occur by nucleus formation and subsequent interface movements, these models usually provide a good fit to the experimental data. However, the order of the transformation (usually first-order) obtained from such models is questionable (*3*).

—geometric models mainly developed for the study of the quartz to cristobalite transition (*14–16*).

None of these models apply to the $\alpha \rightarrow \gamma$ transformation of SnF_2 because of its incompleteness in the range 142 to 174°C. However, the experimental data can be well fitted by the kinetic model of a reversible transformation which can be written as follows:

$$\Phi = [1 - C_\alpha(\infty)] \ln \frac{C_\alpha(t) - C_\alpha(\infty)}{1 - C_\alpha(\infty)} = kt$$

where: $C_\alpha(t)$ = amount of α-SnF_2 at time $t (= 1 - C_\gamma(t))$
$C_\alpha(\infty)$ = "equilibrium" concentration of α-SnF_2 (= amount of α-SnF_2 at $t = \infty$)
k = rate constant.

It is clear that the expression "equilibrium concentration" is used to indicate that the amount of α-SnF_2 does not change any further with time, i.e., as if an equilibrium situation had been reached. It is obvious that there is no thermodynamic equilibrium because a large hysteresis of the transition is observed; all the observations are kinetic effects and not thermodynamic ones. Furthermore, the word "concentration" is used here only by analogy with the homogeneous reactions and does not have any thermodynamic meaning in this transition where all phases are solid. It must also be emphasized that the expression for Φ used here is applied in an empirical manner as the transition is not reversible without hysteresis. This was checked as follows: when no further change was observed at a constant temperature T, the sample was then slightly cooled, but no change in the amounts of α- and γ-SnF_2 resulted.

The rate constant k was obtained at each temperature by least-squares fitting the experimental values of Φ vs time to a straight line (Fig. 3). The activation energy E_a of the transition was subsequently obtained from the Arrhenius equation

$$k = A \cdot \exp(-E_a/RT)$$

A least-squares fitting to the experimental data led to the following values $\ln k = 45(3) - 21.2(1.5) \cdot 10^3/T$ giving an activation energy E_a = 10.7(7) kcal/mole (Fig. 4).

2.2. *Transition Phase*

Many studies (*14–19*) by D.T.A. and

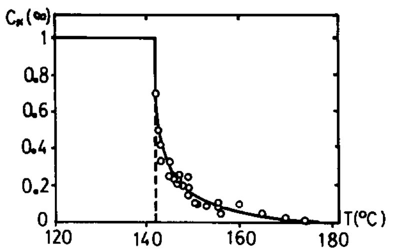

FIG. 2. α- to γ-SnF_2 transition: amount at α-SnF_2 in sample at $t = \infty$ vs temperature.

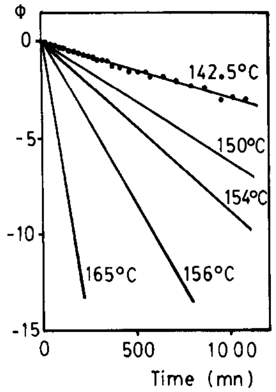

FIG. 3. α- to γ-SnF_2 transition: plot of Φ vs time at different temperatures. Solid lines are least squares fitted.

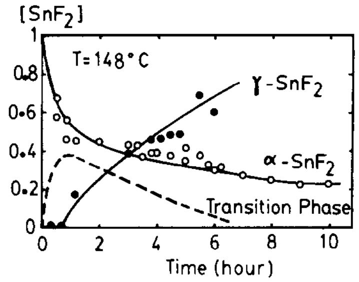

FIG. 5. α- to γ-SnF_2 transition: amount of α- and γ-SnF_2 (solid lines) in the sample vs time. The concentration of "transition phase" is calculated by difference (dotted line).

powder X-ray diffraction of the quartz → cristobalite transition suggested that the transformation involved intermediate amorphous phase usually called "transition phase." It must be outlined, however, that Kuelmer and Poe (*20*) could not detect any amorphous SiO_2 rings in their single crystal X-ray diffraction study of this transition and that there is no direct evidence of the existence of such a phase. We wished to see whether such a "transition phase" occurred as an intermediate step in the α- to γ-SnF_2 transformation. In order to do this, we measured simultaneously the proportion of α and γ phases in the same sample as a function of time; the experiment was done at a single temperature (T = 148°C). There is no problem of differential absorption of X-ray by the different phases present in the samples as they both (α- and γ-SnF_2) have the same composition.

The results are given in Fig. 5: during the initial stages (i.e., about 1 hr), a non-negligible amount of SnF_2 (~50%) disappears whereas no γ-SnF_2 is yet observed in the sample; during the later stages, γ-SnF_2 is forming faster than α-SnF_2 is decaying. Hence this suggests the existence of an intermediate phase in the transition from α- to γ-SnF_2. As no new peaks are observed on the X-ray diffraction pattern this "transition phase" is probably made of very small crystallites. This assumption is furthermore supported by the following experiment: a sieved sample of α-SnF_2 (grain size 125–160 μm) was transformed to γ-SnF_2 at 180°C under dry nitrogen; sieving of the transformed sample then revealed that more than 10% of the particles were smaller than 125 μm, 2% being smaller than 40 μm; moreover an optical examination of the main fraction (125–160 μm) under a microscope showed that these particles are in fact an aggregate of much smaller particles. This transition then gives rise to a considerable fractioning of the crystals and the occurrence of an amorphous phase as an

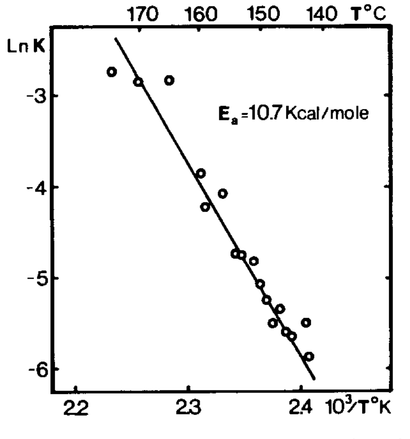

FIG. 4. α- to γ-SnF_2 transition: Arrhenius plot.

intermediate step in the transition, although not directly evidenced, is likely.

2.3. Influence of Grain Size

Preliminary investigations of this transition by D.T.A. (*4*), D.S.C. (*21*), and microcalorimetry (*22*) gave a considerable scatter of results both for temperature (141°C $\leq T \leq$ 167°C) and the latent heat ($45 \leq \Delta H \leq 180$ cal mole^{-1}) of the transition which led to suspect the influence of α-SnF_2 particle dimensions. D.T.A. experiments were then performed with 10 carefully sieved samples with particle size ranging from less than 40 μm up to 300 μm. We observed (Fig. 6) that the temperature at which the transition starts increases when crystallites become smaller (quasilinear dependence); an opposite behavior was observed for the quartz → cristobalite transformation (*19, 23*). One also observed that D.T.A. peaks become broader when the average grain size increases and, for the larger particle sizes, the D.T.A. signals are apparently a superposition of many peaks occurring at different temperatures (Fig. 7). This is further supported by D.T.A. experiments on single crystals (crystal dimensions: 10 to 30 mm³): we no longer observed a single broad peak but a succession of very narrow peaks (Fig. 7). The number of peaks as well as the temperature at which they occur vary from crystal to crystal. Optical examination of partly transformed crystals under a microscope revealed that the transition starts from crystal edges on which one observes white outgrowths of β-SnF_2 while the bulk of the crystal is still transparent and untransformed.

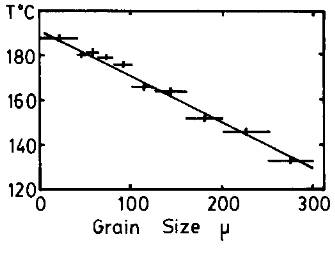

FIG. 6. α- to γ-SnF_2 transition: transition temperature (beginning) vs grain size.

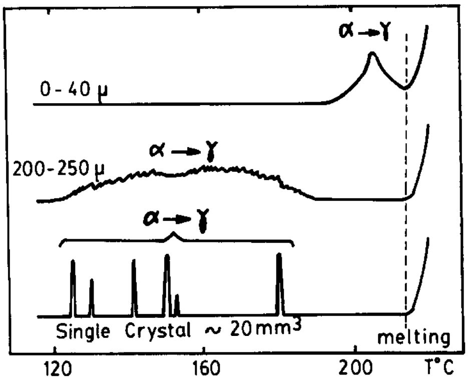

FIG. 7. α- to γ-SnF_2 transition: changes of D.T.A. peak shapes with particle size.

X-Ray irradiation (Cu radiation) as well as annealing (in the range 120 to 160°C depending on sample) do not modify the position or shape of D.T.A. peaks.

3. γ, β- to α-SnF_2 Phase Transition

Although γ-SnF_2 can be kept metastable below the $\alpha \rightarrow \gamma$ transition temperature and its distorted form (β-SnF_2) can be quenched, we often observed a partial or total transformation of γ (or β) to α during cooling or at room temperature (*4*). The same was observed by electrical measurements (*24*): at constant temperature, the electrical conductivity increased progressively from the value of γ-SnF_2 up to a limiting value σ_{lim} intermediate between that for $\sigma_{(\alpha)}$ and $\sigma_{(\gamma)}$; σ_{lim} depends upon temperature.

The powder X-ray diffraction experiments were carried out as described for the α to γ transition. However because of the sluggish nature of the γ, $\beta \rightarrow \alpha$ transition, for some samples, when the transition did not start spontaneously, it was induced by applying a pressure of 500 to 1000 kg/cm² to the pellet for several minutes. After this treatment, the transformation would usually start after 1 or 2 hr. No difference was found between the kinetics for the induced compared to the noninduced samples. For the same reasons, no D.T.A. study could be made, and we could not look for the existence of an intermediate transition phase as was the case for the α to γ transition, because it was not possible to transform completely the sample to α-SnF_2 without moving it out of the furnace and therefore changing the temperature and conditions of recording the data. Hence it is not possible to know the amount of α–SnF_2 in a partly transformed sample.

The X-ray diffraction experiments were performed as a function of time at the following temperatures (°C): 20, 40.5, 66, 90, 104. As for the $\alpha \rightarrow \gamma$ transition, the transformation is not complete over the temperature range explored; an equilibrium situation seems to be reached, depending on the temperature (Fig. 8). Again the experimental data could be fitted by the kinetic model for the reversible transformation defined above. Once more this expression is applied in an empirical manner as the transition is not reversible, and the observations are kinetic effects and not thermodynamic ones. By least-squares fitting the experimental values Φ vs time to a straight line, the rate constant k was obtained which does not seem to obey the Arrhenius equation; therefore no activation energy could be calculated. Another difference with the $\alpha \rightarrow \gamma$ transition is the long time of transformation: for the $\alpha \rightarrow \gamma$ transition no further change is observed after ~24 hr at 142°C while a transformation $\beta \rightarrow \alpha$ was observed at room temperature over more than 6 weeks.

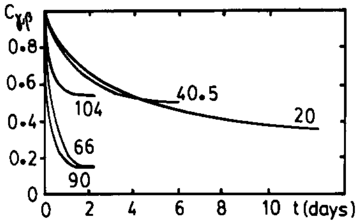

FIG. 8. β, $\gamma \rightarrow \alpha$-$SnF_2$ transition: amount of β, γ-SnF_2 in sample vs time for a few temperatures.

4. Discussion

The experimental results that we have presented above on the $\alpha \rightarrow \gamma$ and $\beta, \gamma \rightarrow \alpha$ transitions of SnF_2 provide information on the incompleteness over a wide temperature range, the temperature dependence of the limiting amount of α-SnF_2 ($\alpha \rightarrow \gamma$) or β, γ(β, $\gamma \rightarrow \alpha$) transformed, the probable existence of an amorphous phase as an intermediate step in the transition, the grain size dependence of the transition temperature as well as the latent heat and the shape of the D.T.A. peaks.

It was claimed by Mryukh (*2, 3*) that the notion of a "velocity of transition" is inapplicable, that the results are independent of time, and that in kinetic studies of solid state transformations, that is warming up the sample rather than the rate of transition which is being measured. Our observations cannot be explained on the assumption that we are measuring the rate of sample warming up for the following reasons:

—for the $\alpha \rightarrow \gamma$ transition: the hexagonal → orthorhombic transformation for $AgNO_3$ we followed at 167°C was complete in less than 30 mn; the transformation of SnF_2 takes place over 2 to 25 hr in the temperature range 142 to 175°C. Hence the long time of transformation for SnF_2 cannot be attributed to the sample warming up.

—for the $\beta \rightarrow \alpha$ transition, the transformation was followed for more than a month at room temperature. In this case, there is no sample warming up, or cooling down, as the transformation occurs at room temperature.

The incompleteness of the transition over a wide temperature range, the temperature dependence of the limiting amount of the phase transformed as well as the influence of the grain size can be explained by the mechanism proposed by Mnyukh (*2, 3*) for three-dimensional nucleation in a crystal: "nucleation occurs only at crystal defects which were present in the crystal and the polymorphic transition temperature is "pre-coded" in the defect. For the different particles of a powder sample, these temperatures will be different." It follows that for a given temperature within the range explored, only the crystallite of which the "pre-coded" temperature is lower than the actual temperature of the sample transform. For the smallest sized crystals, only high "pre-coded" temperatures are present from which the D.T.A. peaks occur at high temperature and which are quite narrow. For the largest sized crystals, the "pre-coded" temperatures are lower. When the sample is heated, the transition starts; new defects with different "pre-coded" temperatures are created following the fragmentation of the crystallites from which broad D.T.A. signals originate which are the superposition of many peaks occurring at different temperatures. The results obtained on single crystals can be explained by the presence of several types of defects with different "pre-coded" temperatures. The experiment shows that these defects are located on the edges of the crystals. Even Mnyukh (*2*) noticed that in monocrystalline samples a "transition range" which brings the transition to a halt can be observed. Continuation of such a transition requires new nucleation that can occur only after some heating. After the next stop a further temperature increase is required, and so on up to complete transition. Similar phenomena are observed in the γ, $\beta \rightarrow \alpha$-SnF_2 transition upon cooling. The high rates of transition observed around 66°C can be attributed to the destabilization of the metastable phases (γ, β) at the $\beta \rightleftharpoons \gamma$ phase transition. This assumption is reinforced by the usual behavior of solids at ferro-paraelastic phase transitions (strong internal strain, high thermal vibrations of atoms) (*25*) although our recent study of the $\beta \rightleftharpoons \gamma$ transition of SnF_2 by neutron diffraction and ^{19}F NMR (*26*) shows no abnormal increase of the Debye–Waller factor of the anions and no motional narrowing of the NMR resonance line in the vicinity of the transition.

Some light can be shed upon the presence of the amorphous "transition phase" as an intermediate step in the $\alpha \rightarrow \gamma$ transformation as well as the considerable fragmentation of crystallites at the transition if one considers the large difference between the crystal structures of α-SnF_2 and β (or γ). When the crystal structure of the α-phase is made from isolated Sn_4F_8 tetramers, β- and γ-SnF_2 structures are built up from infinite networks of Sn_6F_6 rings. We recently showed (*4*) that the $\alpha \rightarrow \gamma$ transition involved a strong displacement of the fluorine atoms as well as a large reorientation of the lone pairs whereas the motion of tin atoms is quite small. Some Sn–F bonds are broken and some new ones appear. It results that this transition is a reconstructive one according to the classification suggested by Buerger (*27–29*) as it involves changes in primary coordination. Indeed, while SnF_3E tetrahedra and SnF_5E *octahedra* (E = lone pair) are observed in α-SnF_2 (6), γ-SnF_2 exhibits SnF_4E *trigonal bipyramids* (*7, 26*). The bonds in the first coordination sphere are broken and reformed. Such transformations involve high energies of activation and are often sluggish. In view of the drastic rearrangement that the structure undergoes, it is obvious that a single crystal of α-SnF_2 cannot remain single through the transition and that fragmentation must occur. We showed that this fragmentation is very important, and it is likely that it has to go down almost to the molecular level. But it is possible that crystallites of a few unit-cell parameters each way can already relax the lattice strain sufficiently to make it through the transition. The same holds for the $\beta, \gamma \rightarrow \alpha$ transition. As fragmentation of single crystals occurs very rapidly, we could not observe for the $\alpha \rightarrow \gamma$ transition movement of the interface between the parent phase and the daughter phase as described by Mnyukh (*2, 3*). Probably many interfaces appear at the same time, resulting from the nucleation at different types of defects of which "pre-coded" temperatures are very close.

The breaking of crystals can also be attributed to the increase in molecular volume (+1.78%) at the $\alpha \rightarrow \gamma$ transition.

The presence of a large hysteresis for the $\beta, \gamma \rightarrow \alpha$ transition upon cooling is in agreement with Mnyukh's results on the inevitability of hysteresis: "It is quite impossible for a phase transition to take place without a finite superheating (or undercooling)."

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