KINETICS OF PHASE GROWTH IN SILVER NITRATE CRYSTALS

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C O N T E N T S

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Growth kinetics of the $AgNO_3$ phase transition were investigated by heating the crystals in a microfurnace, placed on the stage of a polarizing microscope, photographing the transition with a moving-camera, and determining the rate of change graphically.

Linear growth rates, on flat plate single crystals (001) of roughly uniform size (0.5 x 0.5 x 0.05 mm.), were measured in a temperature range of over 200°C. Crystals of bigger and smaller size were used to determine the influence of crystal size on transformation rates. The influence of varied annealing conditions, purity, and decomposition were also checked. Isothermal rates along different crystallographic directions in the same crystal were measured, as well as rates in crystals containing up to 0.3% of $Cd(NO_3)_2$ as impurity. $AgNO_3$ whiskers were grown and their transition rates and properties studied; the bending of whiskers during transition was observed in a few cases. Striations were seen in many crystals during transformation; the presence of strains was verified by X-rays.

The orthorhombic room temperature form could be superheated by about fifteen degrees (actual rates measured up to 11°C superheating), while the trigonal high temperature form was supercooled to any desired temperature by fast cooling. On superheating the crystals nucleated spontaneously, while on supercooling they were nucleated artificially with a room temperature form $AgNO_3$ crystal. The rates

were, on the whole, constant with time, but rose exponentially with temperature on superheating, while on supercooling they rose at first, reaching a maximum, (0.394 mm./sec. at ΔT = 58.5 deg.) then fell exponentially to zero (at about -30°C).

Linear growth rate equations for solid reaction were applied to the experimental results; and as found by other workers the equations gave a reasonable value for the activation energy far away from the transition point (21.1 kcal./mole) but changed to negative values near the transition on supercooling; on superheating a varying activation energy, decreasing with increasing superheating was obtained. The experimental rates were also much faster than predicted by most of these equations.

Since the presence of strains was observed experimentally Turnbull's growth rate equation, which is derived from the absolute reaction rate theory, was modified by adding a strain energy factor to the free nergy term; this correction resulted in a single valued activation energy throughout the whole temperature range for both transitions. On supercooling close agreement between theoretical and experimental growth rates was obtained. The merits and deficiencies of the various growth rate equations are discussed in the light of the experimental values obtained.

DECLARATION

This thesis describes my own work, carried out by me between February 1960 and December 1961. It contains no material previously published, or submitted for a degree, by me or any other person, except where due reference is given.

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GENERAL INTRODUCTION

It was known to men since antiquity that metals when subjected to various heat treatments changed their physical properties to a very remarkable degree. In fact annealing and cold working of metals were the standard techniques known and practiced by men from the dawn of history. But though these changing properties of metals were known and made use of extensively they were not understood; no theories explaining these changes were in existence, nor was it clear what was happening exactly in the metals to account for their changing properties. The science of metallurgy was purely empirical.

Since the European Renaissance broke man free from scholasticism and inspired him to explore and probe into the universe around him, the inquiries by natural philosophers into the nature of our world became more numerous. The advancement of chemistry from the seventeenth century onwards, the discoveries of new chemical substances and their properties, soon brought to light the fact that not only metals change their physical properties on heating but that many organic and inorganic substances do so as well. The systematic study of these phase changes by chemists and physicists soon changed the empirical science of metallurgy into a science proper.

The discovery of the microscope and X-rays enabled scientists to elucidate the microscopic structure of solids so that they can now observe and even predict phase changes and their likely properties.

Since these structure changes in solids are of great commercial importance, as well as being a challenge to the natural philosopher, various workers have studied them both experimentally and theoretically. The results, unfortunately, are by no means simple or easy to elucidate.

Hartshorne, in a series of papers entitled "Studies in Polymorphism" from 1930 onwards, studied the kinetics and mechanisms of a number of phase transitions in solids. He measured the linear growth rates on polycrystalline films, making many perplexing discoveries. He observed, for example, that the growth rates at a constant temperature declined with time for o-nitroaniline[1] and HgI_2[2] but were constant for the sulphur transition.[3,4,5] He also found that thinner films gave faster rates for o-nitroaniline, but slower rates for HgI_2 and S. Also in the sulphur transformation the tiny crystallites showed preferred orientations, leading to different speeds of transitions, or in other words displaying anisotropic growth rates. The growth rates were also dependent on the previous thermal history of the sample.

Erofeev and Mitskevich in three papers published in 1950 and 1952[6] studied the kinetics of NH_4NO_3 III $\rightleftharpoons$ IV transformations by dilatometry. They found that the rates of transition were very much dependent on the temperature and time of annealing their samples before transformation: the rates decreasing with greater annealing time and the more temperature of annealing was removed from the transition point. They also found that decreasing the crystal size

of their samples, whether by grinding or recrystallising, increased the rates of transition by two to three times for the IV $\rightarrow$ III transition and decreased the rate for the III $\rightarrow$ IV transition. Whether these effects were due to different nucleation rates or growth rates, however, could not be established with dilatometry. Hartshorne's polycrystalline films also could not establish beyond any doubt, whether the different growth rates were owing to some intrinsic properties of the crystals, or merely to film shrinkage, gaps between individual crystallites, or some such effects.

Baram[7] in 1956 measured the linear growth rates on single crystals of HgI_2 and found the rates to be twice as fast as Hartshorne obtained for polycrystalline films. He also found the rates constant with time against Hartshorne's decreasing rates. Observations under different magnifications also gave different growth rates at low temperature but almost the same rates at higher temperature ($82^{\circ}C$). Crystals obtained from alcoholic solutions gave smaller rates by half. Thus Baram's work showed further the complex phenomenon of structure changes in solids, and more thorough investigation was indicated if a more detailed understanding of these transformations was to be achieved.

Turning to the mechanisms of phase transitions Hartshorne found that the activation energies for all the substances he studied, except HgI_2, had values comparable with those for the heats of

sublimation of the unstable phase, and hence he assumed that the activated state is a vapour phase, the mechanism being presumably analogous to crystal growth from the vapour. This interpretation, however, only agrees with experimental results for transformations from the higher to the lower temperature form i.e. on supercooling, and there only at temperatures past the maximum i.e. when the rates decrease with decreasing temperature, for near the transition temperature the activation energies change to negative values.[8] The activation energies on superheating usually give values which change smoothly with temperature, decreasing with increasing temperatures. Also the growth rates observed are much too high for such a mechanism; and this mechanism, as envisaged by Hartshorne, only applies to non-metallic transitions.

The anomalies in the activation energies and growth rates are present irrespective of whether the mechanism postulated is the growth of the new phase from the vapour state as two dimensional nucleation (perfect crystal growth, Dunning), or growth on screw dislocations. Turnbull's growth rate equation, derived from the absolute reaction rate theory, which does not assume any specific activated state, gives similar results for the activation energy but a better agreement as to the actual speed of transition. Thus the mechanism of phase transitions seems to be far from being completely elucidated and further investigations are necessary.

To study these various aspects of phase transitions in solids further $AgNO_3$ was selected because it has a transition at 160°C., can be obtained in thin single crystal plates, as well as whiskers, and it can be both superheated and supercooled over a wide temperature range. Conditions known to influence the transition rates were examined, activation energies calculated, and growth rate equations modified to give constant activation energy values both on supercooling and superheating.

CHAPTER I STRUCTURE CHANGES IN SOLIDS

INTRODUCTION

Solid substances usually do not possess the same crystalline form at all temperatures and pressures, but tend to change to a structure with the minimum Gibbs free energy. At absolute zero the form with the minimum heat content is the stable one, but at temperatures above absolute zero the entropies of various substances change rapidly until at some given temperature a different crystalline form may have a smaller free energy, though a higher heat content, and hence a solid substance will change to this new form. The immediate conversion to this new form may, however, be prevented by the energy barriers opposing the transformation, and thus a substance may exist in a metastable phase for a time which may vary from a fraction of a second to geological times.

The driving force in the conversion of one crystalline structure into another is the free energy difference between the phases. The initial formation of the new phase, or the appearance of the nucleus of the new phase, involves an energy input, while the subsequent change into the new phase releases energy. This initial energy expenditure necessitates the subdivision of the overall transition of one crystalline form into another into two distinct processes called nucleation and growth. Nucleation deals with the initiation of the new phase, or the formation of embryos, while growth concerns itself with the subsequent growth of the new phase.

Phase transitions as such are of several types, depending whether the transformations involve the weakening or a complete change of bonds between individual atoms. Structurally the least drastic kind of transition involves no change in the first coordination of atoms, the change being only in the non-nearest neighbours. This transformation type may be of two kinds, viz. displacive, having no rupture of bonds but only a distortion of them (very fast), and reconstructive when higher coordination bonds change, while first ones are retained (sluggish).

Another transformation type is the transformation of disorder, which again may be rotational, breaking of weaker bonds and rotation about strong ones, and substitutional, atoms with broken weak bonds drift and attach themselves to others with stronger bonds. A more drastic type of transformation involves the change of first coordination atoms; which again may be dilatational, achieved by a mere shift of atoms, owing to differential dilatation (rapid), and reconstructive, where first order coordination bonds are broken and then new ones formed (aragonite $\longrightarrow$ calcite). Transformations like the diamond $\longrightarrow$ graphite transition involve a change of bond type i.e. the bonds are different in the two forms; they are usually sluggish.

The two phases during a transformation may possess some atomic fit across the interface, in which case the phase change is called a

coherent transition, or the phases may be separated by an amorphous interface, when the change is called an incoherent transition. The boundary between the phases may be regarded theoretically as sharp or diffuse.

Coherent transitions occur usually in metals where the rigid contact between the phases is not broken; the transformation consisting only in the expansion or contraction of one or more crystallographic direction, and resulting in a new crystalline structure i.e. a phase change. These transitions are usually very fast and presumably require a low activation energy. Incoherent transitions are common in organic and inorganic materials, though inorganic substances may be partly coherent.

Transformations are also called diffusionless, when the rate of transition is not dependent on the diffusion of atoms across the interface, and diffusion controlled when they are. These various types of transitions are discussed by Buerger.[9]

The rate of growth of one phase into another, or the linear movement of the interface, is predicted theoretically by a number of rate equations in existence, usually based on experimental results. These equations postulate a given mechanism for a given transition, assuming the nature of the activated state, and the driving force for the transition.

The mechansims and kinetics of structure changes in solids will next be discussed in a more detailed and systematic way.

PART A. MECHANISMS AND KINETICS

1. NUCLEATION

The term nucleation describes the initiation of a new phase, as distinct from the subsequent growth of it.

The formation of a nucleus of a new phase, as mentioned previously, involves an energy input so that the appearance of a nucleus seems at first glance to be somewhat unlikely. The formation of a nucleus is, however, possible because small elements of a phase do not possess a constant density and energy with time, but change continuously, even though the macroscopic phase is in perfect equilibrium. These fluctuations are always forming and destroying embryos, which under special conditions may become large enough to initiate a transition to a more stable state.

Thus we see that phase transitions in solids are possible, but to find a theory which would account for these transformations in a quantitative way is extremely hard, owing to the difficulty of experimental investigations and to the lack of theoretical estimates of the numerical factors which influence the formation of nuclei in solids.

The theoretical equation describing the rate of nucleation of a new phase in solids is based upon a nucleation rate equation for the formation of a liquid from a vapour phase. The theory explains the presence of the initial energy barrier on nucleation as owing to the fact that the first appearance of a new phase, inside the

mother phase, is accompanied by the formation of a surface, and consequent surface energy. It is this surface energy which constitutes the energy barrier.

The difference in free energies between the element of the new phase and the mother phase (ΔG) is the difference in chemical free energies (ΔG_v) between the two phases in bulk, plus the surface free energy (σ) of the new phase; or assuming a spherical volume element of the new phase of radius (r)

$$\Delta G = 4\pi r^2\sigma + \frac{4\pi r^3}{3}\Delta G_v \qquad (1)$$

With increasing size of the element of the new phase ΔG will at first rise to a maximum positive value and then fall and change to negative values. This implies a maximum positive energy, as well as a point of inflexion, which makes it possible to differentiate the above equation with respect to the radius of our element of the new phase and equate to zero

$$\frac{d(\Delta G)}{dr} = 0$$

and to get the radius of the element of the new phase, or cluster, which corresponds to the maximum of the energy barrier

$$r' = -\frac{2\sigma}{\Delta G_v} \qquad (2)$$

This small element of the new phase is called a critical size nucleus and the corresponding radius the critical size radius.

Since the critical size radius corresponds to the maximum free energy, clusters with radii smaller than critical size will tend to disappear, while clusters larger than critical size will tend to grow.

To calculate the amount of energy required to form the critical size nucleus we substitute equation (2) in (1) and get

$$\Delta G' \text{ (for nucleus)} = \frac{16\pi\sigma^3}{3(\Delta G_v)^2} \qquad (3)$$

Knowing the energy required to form a critical size nucleus and its size, we can calculate the number present in unit volume (I'), at a given temperature and pressure. This was first done by Volmer and Weber[10] for the nucleation of liquid droplets from the vapour phase.

$$I' = n_o \exp\left(-\frac{\Delta G'}{kT}\right) \qquad (4)$$

where n_o is the number of molecules per unit volume in the vapour at saturation.

The rate of nucleation (R) will be the rate at which critical nuclei acquire extra molecules and become free growing. Hertz-Knudsen equation gives the number of gas molecules striking unit area in unit time (G')

$$G' = \frac{O'P'}{(2\pi mkT)^{\frac{1}{2}}}$$

where O' is the surface area of the nucleus

P' the pressure

hence the nucleation rate (R) of a liquid phase from its vapour is

$$R = \frac{\theta' P'}{(2\pi mkT)^{\frac{1}{2}}} n_o \exp(-\frac{\Delta G'}{kT}) \qquad (5)$$

To find the rates of nucleation in condensed phases Hertz-Knudsen equation cannot be applied, since the mobility of atoms in solids is restricted, the movement itself requiring an activation energy A. Therefore for the rate of nucleation in solids, derived by Becker,[11]

$$R = C \exp(-\frac{A}{kT}) \exp(-\frac{\Delta G'}{kT}) \qquad (6)$$

C being a complicated constant.

The nucelation rate equation, as derived above does not give a good quantitative agreement between theory and experiment, since in solid reactions several of the assumptions postulated do not hold completely. In the theory of nucleation of liquids from the vapour we have considered the free energy, the surface energy, the fluctuations of density, as well as the critical radius of the new phase; but in solids these terms become vague and very difficult to determine. First of all we do not know the free energy of the early nuclei because there is no certainty about its structure. Secondly the surface energy cannot be uniquely defined, since a nucleus in the solid possibly has no definite surface; embryos are coherent with the matrix, and both their composition and atomic configuration gradually merge with the

surrounding lattice. For the same reason the critical radius or size of the nucleus in the solid is not a rigorous concept. This is particularly true since the solid nuclei are seldom spherical. Thirdly the role of fluctuations represents a great departure from the ideal case. For here instead of the fairly simple density fluctuations, fluctuations of chemical composition and of atomic configurations must be considered i.e. the probability of the occurrence of a particular crystalline lattice depends not only on the proper ratio of the various atoms in a certain small volume, but also on their arrangement. Finally one more difficulty is the fact that all crystals, or most at any rate, are imperfect and the defects in the crystal structure will add further complications to an already complex problem.

To measure nucleation rates experimentally is very difficult, since the critical size nuclei are quite small (about 100 molecules for water) and hence not visible; and when they reach a visible size, the nucleation rates become contaminated with growth processes and have to be disentangled from them to yield pure nucleation results. Nucleation rates are also often very slow, especially in small crystals, and hence time consuming. It is likewise difficult to say whether a given nucleation rate is owing to intrinsic properties of a solid i.e. homogeneous, or influenced by crystal imperfections, impurities, and so forth, i.e. heterogeneous. Furthermore since nucleation is a completely random process depending on the fluctuations

of energy and density, due to thermal vibrations, a large number of experimental observations have to be made and treated statistically if any reliable results are to be obtained and valid conclusions drawn.

2. GROWTH

The term growth describes the creation of a new phase, after the formation of the critical size nucleus, or the growth of the new phase when both phases are present, as distinct from the initiation of the new phase.

The theories describing the mechanisms and kinetics of the formation of a new phase, usually assume the presence of an energy barrier at the interface, which implies that the molecules, or ions, when moving from one phase into another, have to receive extra energy, or using the language of the absolute reaction rate theory, an activated complex has to be formed.

For many organic and inorganic phase transitions the experimentally obtained activation energies are of the same order as the heats of sublimation of the unstable phase,[4] so that the growth of the new phase may be considered analogous to the growth of a crystal from its vapour state.

The classical crystal growth theories first developed by Willard Gibbs in 1878,[12] Volmer,[13] and others, assume the growing crystal to be perfect with ideally flat faces; since any surface

irregularity would soon be filled by atoms diffusing along the surface. Therefore growth requires the initiation of a new layer; a nucleation process, similar to the nucleation of droplets from the vapour. This implies that an island monolayer of certain size must initially be formed on the flat face before further growth can occur. This growth will continue until a complete new layer is formed on that face, then stop, until another critical size island monolayer appears, making growth possible again. This means that crystal growth is governed by the rate of formation of island monolayers, or by two dimensional nucleation.

The critical size of an island monolayer will depend on the supersaturation pressure of the vapour in equilibrium with the crystal surface, since a finite size nucleus will have a higher vapour pressure than the infinite crystal. The radius (r) of a critical size nucleus is given by the formula

$$r = \frac{s_o \gamma}{kT \ln p/p_o} \qquad (7)$$

where s_o is the area per molecule in the monolayer

γ the specific free energy of the boundary

p/p_o the supersaturation vapour pressure.

The rate of formation of a critical size nucleus (R) is given by the formula

$$R = \frac{ZS}{s_o} \exp. \left(-\frac{A_o}{kT}\right) \qquad (8)$$

where S is the surface area of a crystal face

Z is the rate of arrival of fresh molecules

A_o is half the total edge free energy of the critical size nucleus.

The above equation predicts that growth should be extremely sensitive to supersaturation and that growth should not occur at supersaturations smaller than about 25%.

Volmer and Schultze[14] in 1930 studied the growth rates of individual iodine crystals and found that with supersaturation greater than 1% growth occurred and that it was directly proportional to supersaturation. The classical theory was unable to explain such behaviour and in 1949 Frank,[15] and Burton, Cabrera, and Frank[16] put forward their theory of growth on imperfect crystals, which was able to explain these experimental observations.

The classical theory of crystal growth assumes that crystals are perfect, but it is now known from X-ray studies and the mechanical properties of crystals as well as from other evidence, that most crystalline solids are imperfect and that some of the imperfections present are dislocations.

If a crystal face contains the end of a screw dislocation growth will not destroy that step but will merely rotate it. Thus the presence of a screw dislocation will eliminate the necessity of nucleation and hence make crystal growth possible at low values of supersaturation. The rate of growth (R) of an imperfect crystal surface is then the number of turns of the dislocation spiral passing a fixed point in unit time multiplied by the step height (d)

$$R = \frac{dv_o}{4\pi r_c(1 + 3^{-\frac{1}{2}})} \qquad (9)$$

for low supersaturation

where v_o is the rate of advance of a 'straight' step

r_c is the radius of a critical nucleus

and $v_o = 2(\alpha - 1)x_s Z\beta$

where Z is the frequency with which molecules from the equilibrium vapour strike a lattice site in the surface

β a factor which is usually unity in simple cases

$2x_s$ width of the 'diffusion zone'

$\alpha = p/p_o$

Since v_o is proportional and r_c inversely proportional to the supersaturation, the growth rate is proportional to the square of the supersaturation (when this amounts to a few percent or less).

This result is derived on the assumption that the turns of the spiral are so far apart that they do not compete with each other for molecules from the vapour, (low supersaturation). This is no longer true, if they are closer together than twice the surface diffusion distance x_s; a further increase in step density beyond this scarcely contributes to the increase in growth rate, so that growth now becomes proportional to the first power of the supersaturation (high supersaturation). The full expression for growth is

$$R = \beta dZ(a - 1)\left(\frac{x_s}{10r_c}\right)\tanh\left(\frac{10r_c}{x_s}\right) \qquad (10)$$

or

$$R = \beta dZ\left(\frac{\sigma^2}{\sigma_1}\right)\tanh\left(\frac{\sigma_1}{\sigma}\right) \qquad (11)$$

where $\sigma = (a - 1) \doteqdot \ln a$

$\sigma_1 = (10r_c/x_s)\ln a = 10\gamma s_o/x_s kT$

This gives a transition from the parabolic law

$$R = \beta dZ\frac{\sigma^2}{\sigma_1} \qquad (12)$$

at low values

to linear law

$$R = \beta dZ\,\sigma \qquad (13)$$

at high values of supersaturation.

When crystals grow from solution, and not from the vapour state, x_s probably loses its significance and is replaced by the thickness of the effectively unstirred boundary layer of solution at the crystal surface. The fundamental approach, however, is not changed so that the same general considerations, as used for crystal growth from the vapour, apply.

Some of the theories of growth rates in phase transitions assume a vapour or liquid intermediate state, and the subsequent growth of the new phase is taken as perfect or imperfect crystal growth from that intermediate state. Several of these theories will now be discussed in a more detailed and systematic way.

PART B. LINEAR GROWTH RATE EQUATIONS

1. HARTSHORNE'S LINEAR GROWTH RATE EQUATION

In 1935 Hartshorne[1] studied the transformation of α to β-o-nitroaniline and found the activation energy for that process to be of the same order of magnitude as the latent heat of sublimation of the unstable phase. He, therefore, postulated that the linear rate of advance of the interface was equal to the difference between the rates of escape of molecules from the two crystal lattices, these rates being the same as the rates of evaporation of the crystals into a vacuum. Later work on the yellow to red mercuric iodide transition has cast some doubt on this mechanism; however, a rate equation can

be derived just as well even if the activation energies are not equal to the heat of sublimation.

In deriving his rate equation Hartshorne[8] assumed that the interface between the two lattices consists of a thin transitional layer of the order of one molecule in thickness, composed of molecules of high energy in a state of disorder. Molecules escape from each lattice into this layer as they acquire sufficient energy. They then stand an equal chance of either returning to their parent lattice or of condensing on the opposite side, i.e. the probability that a molecule which breaks free from one crystal modification will contribute to the growth of the other is $\frac{1}{2}$.

Let us consider first the transformation of an enantiotropic substance below the transition point. Then if v_1 is the rate of escape of molecules from the unstable form, and v_2 that from the stable form, both multiplied by the appropriate factor to convert them to linear rates of recession of the crystal surfaces, we have that v, the linear rate of advance of the interface, is given by

$$\begin{aligned} v &= \tfrac{1}{2}(v_1 - v_2) \\ &= \tfrac{1}{2}(A_1 e^{-E_1/RT} - A_2 e^{-E_2/RT}) \end{aligned} \qquad (14)$$

where E_1 and E_2 are the activation energies of escape, and A_1 and A_2 are factors which depend on the vibration frequencies of the molecules in the crystals and which to a first approximation may be taken as independent of temperature.

Now $$E_2 = E_1 + q,$$

where q is the heat of transformation. Substituting for E_2 in (14) we obtain

$$v = \tfrac{1}{2}e^{-E_1/RT}(A_1 - A_2e^{-q/RT}) \qquad (15)$$

But at the transition point T_o, v = 0. Therefore

$$A_1 = A_2e^{-q/RT}$$

or $$A_2 = A_1e^{q/RT}$$

Substituting for A_2 in (15), we obtain

$$v = \tfrac{1}{2}A_1e^{-E_1/RT}(1 - e^{q/R(1/T_o - 1/T)}) \qquad (16)$$

It is assumed that q, E_1 and E_2 are independent of temperature.

According to this equation, v passes through a maximum value, as is observed in practice. We may obtain a value for the temperature, $T_{max.}$, at which the velocity has this maximum value by differentiating v with respect to T and equating to zero, whence

$$T_{max.} = 1/[\,1/T_o + \tfrac{R}{q}\ln(1 + q/E_1)\,] \qquad (17)$$

Equation (16) may be put in the following logarithmic form:

$$\ln v - \ln (1 - e^{q/R(1/T_o - 1/T)}) = -E_1/RT + \ln A_1/2 \qquad (18)$$

From this it is seen that the plot of the difference between $\ln v$ and $\ln (1 - e^{q/R(1/T_o - 1/T)})$ is a straight line with a slope of $-E_1/R$. Hence the activation energy can be determined.

Equation (16) may be modified to apply to an enantiotropic transformation above the transition point simply by changing the sign of the quantity in the brackets, thus:

$$v' = \tfrac{1}{2}A_1 e^{-E_1/RT}(e^{q/R(1/T_o - 1/T)} - 1) \qquad (19)$$

The subscript 1 still refers to the form which is unstable below the transition point, now the stable form, and T is now greater than T_o. The equation corresponds to a continuous increase of the linear rate v' with rise of temperature.

From the general thermodynamic relation G = H - TS, where G is the free energy, H the heat content, and S the entropy, follows, assuming q (= $-\Delta H$) to be a constant, that equation (16) can be put in the following form:

$$v = \tfrac{1}{2}A_1 e^{-E_1/RT}(1 - e^{\Delta G/RT}) \qquad (20)$$

since $$q\,\frac{T_o - T}{T_o} = -\Delta G.$$

By expanding the exponential term inside the brackets in equation (16) and neglecting all but the first two terms of the expansion, we obtain

$$v = \tfrac{1}{2}A_1 q/RT\ \frac{T_o - T}{T_o}\ e^{-E_1/RT} \qquad (21)$$

and for equation (20) we obtain

$$v = \tfrac{1}{2}A_1\ \frac{(-\Delta G)}{RT}\ e^{-E_1/RT} \qquad (22)$$

This approximation is a close one only if q is small and T is not too far below T_o.

Equations (20) and (22) show that the difference between the free energies of the two modifications is the 'driving force' in a phase transformation.

2. DUNNING'S EQUATION

Dunning[17] suggested a somewhat different growth rate equation from Hartshorne's, in which he considers the growth of the new phase to be analogous to perfect crystal growth from the vapour. He assumes that the transitional layer between the two lattices behaves

as a true vapour and that the rate of advance of the interface depends not only on the supersaturation of the vapour with respect to the stable phase, but also on the probability of formation of two-dimensional nuclei on the plane surface of this stable phase.

To calculate the rate of growth of a new phase Dunning uses Volmer's equation (18) for the linear rate of growth of a crystal from its vapour. In a simplified form, it is:

$$v = K\, e^{-E/RT}\, e^{-A'/RT} \qquad (23)$$

where E is the activation energy for the escape of molecules from the unstable lattice (i.e. the internal latent heat of sublimation)

A' the activation energy for the formation of two-dimensional nuclei

K a constant

but

$$\frac{A'}{RT} = \frac{\omega M \rho^2 N T_o}{2qd\delta RT(T_o - T)} = \frac{\text{const.}}{T(T_o - T)}$$

where ω is a shape factor

M is the molecular weight

ρ the edge free energy

N the Avogadro number

q the heat of transformation

d the density

δ the spacing between lattice planes.

Substituting for A'/RT in equation (23) we obtain;

$$v = K.e^{-E/RT} e^{-\frac{\text{const.}}{T(T_o - T)}} \qquad (24)$$

or taking logarithms

$$\ln v = \ln K - \frac{E}{RT} - \frac{\text{const.}}{T(T_o - T)} \qquad (25)$$

which enables the activation energy to be found.

The chief difference in Dunning's equation, as compared to others, is that it points out that surface nucleation may be the rate determining factor in solid - solid reactions.

3. BRADLEY'S EQUATION

Bradley[19] in 1956 postulated another growth rate equation for solid-solid transformations, assuming, as Hartshorne and Dunning did, a vapour transition state. To obtain a simple picture for the transition, he imagined the conversion brought about via the vapour phase in an enclosure which contains the two solid phases, so that the rate depends on the "affinity".

If a_1 and a_2 are the evaporation coefficients, and p_1 and p_2 the saturation vapour pressures of the two solids a and b, of which

the latter is unstable at temperature T, then for equality of loss and gain of vapour

$$\frac{(a_1 p_1 + a_2 p_2)}{(2\pi mkT)^{\frac{1}{2}}} = \frac{(a_1 p + a_2 p)}{(2\pi mkT)^{\frac{1}{2}}} \qquad (26)$$

where p is the vapour pressure in the vessel, k is the Boltzmann constant, m the molecular mass, and it is assumed that the solids have equal surface areas exposed to the vapour. It follows that

$$p = \frac{(a_1 p_1 + a_2 p_2)}{(a_1 + a_2)} \qquad (27)$$

The rate of the solid — solid reaction in molecules cm.$^{-2}$ sec.$^{-1}$ is therefore

$$v = \frac{a_1 (p - p_1)}{(2\pi mkT)^{\frac{1}{2}}} = \frac{a_1 a_2 (p_2 - p_1)}{(a_1 + a_2)(2\pi mkT)^{\frac{1}{2}}} \qquad (28)$$

If d is the density of the 'a' phase, the linear rate for this phase is vm/d cm. sec.$^{-1}$.

To a first, and often very good, approximation

$$p_2 = B_2 e^{-E_2/RT}, \quad \text{and} \quad p_1 = B_1 e^{-E_1/RT} \qquad (29)$$

where the B's are the so-called temperature independent factors (related to entropies of vaporisation) and the E's are the latent heats of sublimation.

Hence the rate of the solid $\longrightarrow$ solid reaction is given by

$$v = \frac{a_1 a_2}{(a_1 + a_2)} \quad \frac{B_2}{(2\pi mkT)^{\frac{1}{2}}} \quad e^{-E_2/RT}(1 - e^{\Delta G/RT}) \tag{30}$$

since

$$-\Delta G = RT\ln(p_2/p_1) \tag{31}$$

assuming that the vapours are perfect gases.

Equation (30) holds whether or not there is a transition point. For enantiotropes $\Delta G = 0$ at the transition temperature T_o, in agreement with equation (30). If this equation is rewritten in the form

$$v = \frac{a_1 a_2}{(a_1 + a_2)} \quad \frac{1}{(2\pi mkT)^{\frac{1}{2}}} \quad (B_2 e^{-E_2/RT} - B_1 e^{-E_1/RT}) \tag{32}$$

the condition at the transition point makes

$$B_2 e^{-E_2/RT_o} = B_1 e^{-E_1/RT_o} \tag{33}$$

which gives

$$v = \frac{a_1 a_2}{(a_1 + a_2)} \quad \frac{B_2}{(2\pi mkT)^{\frac{1}{2}}} \quad e^{-E_2/RT} \left[1 - e^{(q/R)(1/T_o - 1/T)}\right] \tag{34}$$

where q, the reaction heat per mole, is given by $q = E_1 - E_2$.

Equation (34) is similar in form to the one given by Hartshorne.

4. TURNBULL'S EQUATION

Turnbull,[20,21] following the formalism of the absolute reaction rate theory, derived a general theoretical equation for a phase transformation, assuming the density change and component redistribution to be negligible. It is essentially analogous to an equation applied by Mott[22] to crystal growth in recrystallisation.

The theory considers the free energy of atoms moving from phase '1', across the boundary, or interface, and going into phase '2'. Let 'a' and 'b' represent atomic sites in phases '1' and '2' respectively. Atoms in phase '1' will have a different free energy from atoms in phase '2', and since an energy barrier exists between the two phases, atoms at the interface will have higher free energies than in either of the two phases. Then the difference in the free energies between sites 'a' and 'b' is ΔG, the difference in the free energies between the two phases. ΔG_a is the free energy difference between the activated state and phase '2'.

According to the absolute reaction rate theory the jump frequency across the interface will be $\nu = kT/h$. Then frequency of an atom jumping from phase '2' into phase '1' is

$$f_{21} = kT/h \exp(-\Delta G_a/RT)$$

and the jump frequency of '1' to '2' is

$$f_{12} = kT/h \exp[-(\Delta G_a + \Delta G)/RT]$$

Therefore the net transfer of atoms across the interface

$$f = f_{21} - f_{12} = kT/h \exp(-\Delta G_a/RT)\,[1 - \exp(-\Delta G/RT)] \qquad (35)$$

or

$$f = \frac{kT}{h} \exp\left(-\frac{\Delta G_a}{RT}\right)\,[1 - \exp\left(+\frac{\Delta G}{RT}\right)]$$

if ΔG is taken as negative i.e. in the conventional way for a spontaneous reaction where ΔG (reaction) = G(products) - G(reactants), and the linear rate of growth v of the new phase will be the net rate of transfer of atoms, times the distance they move in each jump, which is the width of the interface λ. Therefore

$$v = f\lambda = (kT/h)\,\lambda \exp(-\Delta G_a/RT)\,[1 - \exp(+\Delta G/RT)] \qquad (36)$$

or

$$v = \sqrt{\lambda} \exp(-\Delta G_a/RT)\,[1 - \exp(+\Delta G/RT)] \qquad (37)$$

but since $\Delta G_a = \Delta H_a - T\Delta S_a$ equation (37) can be expressed as

$$v = \sqrt{\lambda} \exp(\Delta S_a/R) \exp(-\Delta H_a/RT)\,[1 - \exp(+\Delta G/RT)] \qquad (38)$$

These equations are general equations which only assume an energy barrier between the two phases without saying anything about the nature of the interface causing the barrier.

5. MOTT'S 'ISLAND MODEL' EQUATION

Mott,[20] discussing the rates of grain growth and slip at grain boundaries in metals, explained the large pre-exponential factors obtained, by putting forward the hypothesis that grain surfaces in contact can be divided into islands where the fit is reasonably good, separated by lines near which the fit is bad. The elementary act, which allows slip to occur, is the disordering of atoms around each island where the fit is good. Similarly for recrystallisation, the crystals grow at each step by disordering, or melting, of a group of n atoms of one crystal and changing to the structure of the growing crystal. Thus the rates are fast because n atoms move across at once and not single atoms.

Mott's growth rate equation can be derived in the same way as Turnbull's equation, using the formalism of the absolute reaction rate theory (23). We then obtain

$$v = \sqrt{\lambda}\exp(-\Delta G_a/RT)(1 - \exp(\Delta G/RT))$$

and

$$v = \sqrt{\lambda}\exp(\Delta S_a/R)\exp(-\Delta H_a/RT)(1 - \exp(\Delta G/RT))$$

which are the same as equations (37) and (38).

But if we do not know the nature of the activated state, we cannot calculate the value of ΔS_a, and hence the value of the whole pre-exponential factor. However, on the basis of his 'island model'

for recrystallisation, where n atoms move across the boundary simultaneously, Mott has obtained a relation between ΔH_a and ΔS_a. This reduces the number of adjustable parameters to one: n, the number of atoms which melt in the activated process and recrystallise on the other side of the boundary. ΔG_a then becomes the free energy of melting n atoms; and we get the relation

$$\Delta G_a = n \Delta G_m$$

where ΔG_m is the increase in the free energy on melting at temperature T. ΔG_m can be approximated by the relation

$$\Delta G_m = L(1 - T/T_m)$$

where L is the latent heat of fusion, and T_m the melting temperature. Mott then obtains the expression

$$v = \sqrt{\lambda} \exp(nL/RT_m) \exp(-nL/RT) \left[1 - \exp(\Delta G/RT)\right] \qquad (39)$$

This equation has a bigger pre-exponential than previous equations; e.g. the pre-exponential factor $\sqrt{\lambda} \exp(\Delta S_a/R)$ of Turnbull's equation becomes $\sqrt{\lambda} \exp(nL/RT_m)$ and ΔH_a becomes nL.

CHAPTER II MATERIALS AND METHODS

PART A. MATERIALS

1. PREPARATION

Single crystals of silver nitrate, used in measuring the growth rates of $AgNO_3$ phase transition, were prepared by recrystallising Analar $AgNO_3$ three time from conductivity water. The conductivity water was obtained by distilling de-ionised water twice in a two stage distilling apparatus, the first distillation carried out with alkaline potassium permanganate, the second distillation giving water with a conductivity of 10^{-6} ohms^{-1}.

The glassware used was soaked in nitric acid for at least a week, after the usual cleaning with detergents, and then allowed to stand in conductivity water, which was changed periodically to remove foreign ions. The glassware was always kept in pure water, covered with a watchglass, and locked in a glass cabinet.

In purifying $AgNO_3$ the first two recrystallisations were conducted by cooling hot saturated solutions of $AgNO_3$ and filtering the product through a sintered glass crucible. The final recrystallisation consisted of dissolving the purified $AgNO_3$ at room temperature to form a saturated solution, which was put in a desiccator, containing $CaCl_2$, and allowed to recrystallise by evaporation in the dark. Thin flakes of $AgNO_3$ crystals were thus obtained.

Silver nitrate crystals containing known amounts of impurity, mainly cadmium nitrate, were prepared in a similar way. The two salts were recrystallised separately twice, then given weights of the purified silver and cadmium nitrates were put together (usually one atomic percent of Cd), dissolved in water and about one quarter of the original amount was allowed to recrystallise in the dark. The crystals were then taken out, dried, and analysed by X-ray spectroscopy. Perfect crystals of required size were selected and their growth kinetics measured.

2. DRYING

The rates of phase transitions in solids are very often influenced by traces of moisture; therefore thorough drying is necessary if one wants to obtain growth rates, representing the intrinsic properties of a phase transition.

The drying of $AgNO_3$ crystals was conducted, first of all, in a vacuum with a liquid air trap; but this resulted in some decomposition of the crystals, even when dried in the dark. The crystals turned from white to dark, acquiring a silver mirror on the surface. Thus vacuum drying was found to be impractical, and drying in a desiccator over phosphorus pentoxide was tried as a next step. The desiccator was always kept in a dark cupboard, as light is also responsible for decomposition. After leaving the crystals, for several days in the desiccator, however, it was found that P_2O_5 also

decomposes $AgNO_3$ to some extent. Tiny amounts of decomposition could be detected when the crystals were viewed under the polarizing microscope with the Nicols crossed; a somewhat darker and spotted surface was observable in slightly decomposed crystals.

Thus P_2O_5 was also found to be too drastic a drying agent and $CaCl_2$ was finally chosen, as it did not decompose $AgNO_3$ provided the crystals were not dried for long periods of time. Drying time from one to three days was chosen, as prolonged drying tended to result in decomposition and decomposed crystals were found to give higher growth rates.

Since $AgNO_3$ is not a particularly stable compound, it was prepared in small batches, kept in the dark, as much as possible, dried for a few days only, and used before any sign of decomposition could be detected. Decomposed crystals were discarded and new samples prepared using the same experimental conditions.

3. ANALYSIS.

Traces of impurities sometimes have profound effects on reaction rates in solids, e.g. grain growth in metals,[24] and recrystallisation of sodium chloride.[25] Spectroscopic analysis of the crystals used showed them to contain 27 parts per million of impurity; the biggest impurities being silicon 10 parts, and aluminium 5 parts per million. Other analyses showed higher impurity contents sometimes; the biggest impurity being 78 parts per million, (Al 30 parts, Si 20 parts, Mg 20, Ba 4, Ca 3, Cu 1 parts per million).

To check whether purer $AgNO_3$ crystals would have different growth rates, spectrographically standardised crystals, supplied by Johnson, Matthey and Co. Limited London, 1956, were used. The impurity content was: Fe 2 p.p.m., Ca, Cu, Mg, Na, each less than one part per million, and other impurities were not detected at all. These crystals were used straight from the bottle, and also recrystallised once, to give higher crystal perfection; but in both cases the rates were of the same order as in the crystals with the higher impurity content.

Crystals with specially added amounts of impurities were analysed by X-ray spectroscopy for cadmium; the cadmium to silver ratio varied from 0.225 to 0.075 atomic percent. Lanthanum and strontium nitrates were also added as impurities. Only slight increases in growth rates were observed for all the impure crystals.

PART B. METHODS

1. OBSERVATION AND RECORDING

To observe the growth rate of $AgNO_3$ phase transition a Cooke polarizing microscope was used. The purified and dried crystals were selected according to size, keeping roughly to the same dimensions, about 0.5 mm across and 0.05 mm. thick; the crystals were flat plates, with the (001) plane forming the large horizontal surface, as given by Jaeger[26] and others. Crystals of larger size, 1.3 mm. across and 0.07 mm. thick, as well as smaller crystals, 0.15 mm. across and

0.03 mm. thick, were also used. Whiskers, grown on the sides or bottom of a beaker, 0.75 mm. long and 0.015 mm. diameter, were likewise studied.

As the tiny crystals displayed interference colours in polarized light, their thickness was measured by the use of λ - compensating plate, which gave the order of the interference colours, and knowing the birefringence for $AgNO_3$ and the formula $R = h(n_2 - n_1)$, relating relative retardation (R) to crystal thickness (h) and the birefringence $(n_2 - n_1)$, the thickness could be calculated; or using colour charts, given by Chamot and Mason[27] and others, the thickness could be simply read off. The length and breadth of the crystals were measured by photographing the scale of a micrometer slide and thus calibrating the film which was subsequently used to photograph the crystals.

Since the room temperature form $AgNO_3$ is orthorhombic, the (001) plates had the 'a' and 'b' crystallographic directions in the plane of the plates, and these directions were found with the aid of the λ -compensating plate, or quartz wedge, which increased or decreased the interference colours, making it possible to identify the two crystallographic directions. Thus knowing the a and b-axes the growth rates along them were measured. The rates along the 'c' direction were measured on whiskers, since they had their c-axis along the length of the needle.

The crystals were heated to the transition temperature, rather fast at first, but slower as the transition point was approached; the heating rate being not more than one degree per minute in the last stages; the overall heating process taking about half an hour.

At the transition point the movement of the changing interface could be reversed by altering the temperature by about 0.2°C, so that the equilibrium transition temperature could be found accurately. The room temperature form, however, superheated usually by some degrees before it changed spontaneously to the trigonal high temperature form. The amount of superheating varied from a fraction of a degree to about sixteen degrees.

The transformation itself was observed in polarized light with crossed Polars. The crystals were placed in the extinction position so that the 'a' and 'b' crystallographic directions were along the cross-hairs of the eye-piece of the microscope. The transformation was photographed with a Robot camera (35 mm. film), capable of taking a sequence of up to 24 photos on one winding, either as single exposures, or at rates up to 12 frames per second. The magnifications used were X50, X200, and X400, the X20 and X40 objective being special long distance ones. An adapter made it possible to observe the transition and photograph it at the same time.

After the transformation of the room temperature form to the high temperature form was complete, the crystal was heated to a temperature

10° above the transition point, and kept there for 10 minutes to destroy any nuclei of the low temperature form that might still exist, as well as to anneal strains. The annealing time was varied from one minute to one hour, and the annealing temperature lowered to five degrees superheating, to verify whether the annealing conditions have any influence on subsequent transition rates; but no change in growth rates was observed. Rigid annealing conditions of ten degrees superheating and ten minutes annealing, however, were maintained.

After annealing the crystals were cooled quickly, to any desired degree of supercooling, and the transition to the room temperature form was started by nucleating the high temperature form crystal with a crystal of the room temperature form: artificial nucleation was used as the high temperature form could remain unchanged for an inconvenient legth of time, especially when no temperature fluctuations occurred.

The nucleating crystal was attached to a steel needle, the end of which was flattened so that on touching, the crystal adhered to it without any binding. The needle itself was soldered into a brass block, which was screwed to the stage of the microscope and could be moved in two directions by screws. The needle entered the furnace through a groove at the top side, so that the furnace could be covered once the needle was in position. Thus the nucleating crystal could be

manipulated inside the furnace, and made to touch the high temperature form crystal whenever desired.

The transforming crystal was photographed in the same way as the transition on heating, and the movement of the interface measured from successive photographs. The distance travelled by the interface was plotted against time, and the rate of growth of the phase change obtained from the slope of the graph. From four to twenty four photographs were taken for any individual transition. The isothermal rates in turn were plotted against temperature to obtain the variation of growth rates with the degree of supercooling or superheating.

2. HEATING

To make the heating of crystals on the stage of a microscope possible, a special microfurnace had to be constructed. Heating the crystals on a hot stage, or in the loop of a heated wire, was considered unsatisfactory as in these types of heating arrangements considerable temperature gradients exist. The aim was to have the crystals at a uniform and accurately known temperature throughout, so that the growth kinetics observed would represent the true intrinsic rates at equilibrium conditions, and not rates influenced by thermal gradients, temperature stresses, or some such effect. A furnace was therefore constructed which enclosed a crystal on all sides, keeping it at a constant temperature throughout its whole volume, shielded

from draughts, sudden temperature fluctuations, and moisture. The exclusion of moisture is very important, as $AgNO_3$ is extremely soluble in water. If, for example, the tiny crystals were placed in the furnace, say on a rainy day, or first thing in the morning, enough moisture would condense on the crystals to dissolve them. Thus the furnace had to be preheated to drive out moisture before a crystal could be inserted, and the crystals themselves had to be kept in a desiccator over $CaCl_2$ all the time.

The microfurnace built was cylindrical in shape, with a flat top and bottom. The sides had an inner diameter of about 1.2 cm. and an out diameter of about 1.7 cm. and were built from Sauereisen cement; nichrome heater wires were embedded inside the walls. The bottom consisted of two glass layers; two quartz cover slips, the lower one cemented to the bottom of the furnace, and the upper one fitting inside the furnace, resting on a ring of cement. Between the two slides was a copper-constantan thermocouple, shaped in the form of a loop, to measure the temperature. The crystals were placed on the inner slide. The outside of the bottom of the furnace was covered with a piece of asbestos paper, with a hole in the middle to transmit light, and to make sure, in conjunction with the cemented thermocouple, that the crystal was placed always in the same position, thus eliminating any errors in temperature measurement due to the possible temperature gradients in the furnace. The top of the furnace consisted of another

glass cover slip. The height of the furnace was just over 1.2 cm.; the working distance, even with special long distance objectives, was only about 1.5 cm.

The furnace was baked for several days at high temperatures, to harden the cement and to drive out moisture, and it was found to be suitable for temperatures up to about five hundred degrees, or even higher temperatures, if the copper-constantan thermocouple were replaced by a thermocouple capable of measuring higher temperatures. At higher temperatures the optics of the microscope had to be protected from heat by passing cold water through copper coils wound around the objective and substage condenser of the microscope.

3. TEMPERATURE CONTROL AND MEASUREMENT

Heating the microfurnace to the required temperature was accomplished easily by passing an electric current through nichrome wires embedded in its walls. But to control the rate of heating precisely, without any temperature fluctuations, was a far more difficult undertaking. Controlling the temperature with the use of constant voltage transformers, variacs, and rheostats have proved to be far from adequate, and an electronic device, which controls the temperature automatically, had to be built to give the required temperature control; since a temperature fluctuation of $\pm$ 0.2°C. during the transition was sufficient to reverse the transformation completely, if it was very close to the transition temperature, or to make almost meaningless

the rates obtained at temperatures somewhat removed from the equilibrium temperature. One could not, for instance, say whether the isothermal rates decline or increase with time, or whether they are spasmodic in nature. To establish these facts, very precise temperature control was required.

Such temperature control was obtained by building an electronic device, as published by McKeown,[28] though in a slightly modified form. This device incorporates a Wheatstone bridge arrangement, one arm of which constitutes the furnace heater wires, one is a variable resistance, one a controller winding, and one a constant resistance. The galvanometer of the Wheatstone bridge reflects a light on a photocell, which in turn operates a phase sensitive circuit controlling a thyratron which supplies the current to the heater wires of the furnace. By the appropriate setting of the variable resistance the required temperatures and continuous control was obtained.

The temperature controller built differs from the one given by McKeown in that instead of the platinum control windings in McKeown's furnace, a thermopile consisting of four copper-constantan thermocouples in series was used to control the temperature. The thermopile was used to eliminate temperature fluctuations about the required position, due to the period of swing of the galvanometer. The thermocouples of the controlling thermopile were spaced in the furnace in such a way that the signal to switch off the heater current was given gradually, reducing the current first of all, and not cutting it off

all at once, and thus preventing the galvanometer from oscillating around its equilibrium position, and with it the temperature in the furnace. The spacing of the thermocouples reduced drastically the overshooting of the temperature wanted, since one of the thermocouples was placed as close to the heater wires as possible, inside the walls of the furnace, the other two touching the inside walls, and the fourth one was placed more towards the centre of the furnace. The spaced thermocouples thus gradually intercepted the increasing or decreasing temperatures and set a correcting pulse to the controller. This method permitted a temperature control to a twentieth of a degree.

The required temperature was obtained by setting the dials of the potentiometer, connected to the thermopile, to a predetermined value; the potentiometer's galvanometer operating the photocell. The reading of the potentiometer was calibrated against the furnace temperature, so that a given dial setting on the potentiometer corresponded to a known furnace temperature. Temperature increases of $0.05^{\circ}C$. could be made.

For temperatures below room temperature the furnace had to be cooled instead of being heated, and this was accomplished by blowing cold, dry nitrogen gas on the furnace, which was covered with a loose polythene jacket, to make more efficient cooling. Owing to the extreme solubility of $AgNO_3$ in water the nitrogen gas, supplied from a cylinder, was dried by passing it through U-tubes filled with solid $CaCl_2$, and then cooled by bubbling it through liquid air. Depending

on the stream of the cold gas various temperatures were obtained. The lowest temperatures used was -30°C.

The temperature measurement was accomplished with a separate copper-constantan thermocouple, which was cemented in position between the two glass slides forming the double bottom of the microfurnace. The hot junction of the thermocouple, silvered to prevent oxidation, was made into a loop so that the crystal could always be placed in the same position, thus avoiding any possible temperature gradients in the furnace, even though none were detected in the space corresponding to the crystal size used. To check gradients the caesium and rubidium nitrate transitions were used. These transformations do not superheat, and long needles will transform all at one temperature if no gradient in the furnace exist; or alternatively the temperature rise required to change the whole needle will correspond to the temperature gradient in the furnace.

The cold junction of the thermocouple was placed in ice, the voltage read off from a potentiometer, and the corresponding temperature found from tables. This temperature did not, however, coincide with the temperature of the crystal within the furnace, and hence the thermocouple was calibrated using known transition temperatures of caesium, rubidium, and ammonium nitrates (NH_4NO_3 III$\rightleftharpoons$IV transition); these transformations can easily be reversed, and hence they can be accurately determined without any risk of superheating. Other temperatures

were obtained from the known and checked melting points of organic substances e.g. oxalic and phthalic acids etc.. From these calibrations charts were drawn and subsequent true temperatures were obtained from them. Checks were made periodically to see whether any changes have occurred. Absolute temperatures correct to $\pm$ 0.1°C. were thus obtained.

One consideration, important to temperature control and measurement, as well as to the actual growth rates observed during phase transitions, was the amount of heat liberated or absorbed during a transformation. This was especially important in the measurement of isothermal growth rates.

If no conduction of heat away or to the specimen occurred, considerable changes in temperature would be expected; but as the crystals used were extremely small, it was hoped that no great changes in temperature would occur, nor were they found in the $AgNO_3$ transition. Nevertheless some temperature changes might still occur at the changing interface, even though they were not registered by the measuring thermocouple.

A reference to the literature on kinetics of phase changes revealed that the interface of the azoxybenzene transition, studied by Hodkin and Taylor,[29] showed a calculated temperature rise of only 0.03°C., while Hartshorne[4] worked out the temperature rise for sulphur transition to be only 0.02°C. at the maximum growth rates, and experimentally undetectable. Using the equation given by Hartshorne

the temperature rise for $AgNO_3$ transition, at its maximum growth rates, was found to be 0.18°C. But as Hartshorne pointed out the theoretical value is probably in excess of the actual and experimentally observable. Therefore it was concluded that no significant temperature rise occurs at the interface, and no allowance was made for it in measuring growth rates.

CHAPTER III EXPERIMENTAL RESULTS

INTRODUCTION

Niggli[30] found that below 160°C. $AgNO_3$ is orthorhombic, the structure approximating to the centrosymmetric symmetry of Pbca. Kracek[31] and Fischmeister[32] found the higher temperature structure to be trigonal of the calcite type. The transformation is reconstructive, there being no apparent structure relationship between the phases. Bridgman[33] found that the transition has a volume change of 1%, the high temperature form having a higher density, i.e. it contracts on heating and expands on cooling.

The orthorhombic to trigonal phase transition occurs spontaneously at various degrees of superheating, depending on the size of the crystals used; smaller crystals superheating easily up to ten or fifteen degrees, while bigger ones often change when only a fraction of a degree above the transition temperature. On supercooling the crystals were nucleated artificially.

Growth rates will now be discussed in more detail in the following sections.

PART A. $AgNO_3$(II) ⟶ $AgNO_3$(I) TRANSITION

1. GROWTH RATES IN (001) PLATES

(a). ISOTHERMAL GROWTH RATES

The growth rates at a given temperature were found, on the whole,

to be constant with time, more often than not only one nucleus being responsible for the whole transformation, but not infrequently two or three nuclei would appear in succession, forming different crystallites, and often growing at different speeds, especially when the rates were slow, as at low values of superheating. One nucleus, however, was also often responsible for the formation of several crystallites.

The rates were not constant with time for small values of superheating, up to one degree, when they were found often to slow down or even stop, further heating up to half a degree being required to bring the transformation to completion. No such phenomenon was observed at higher values of superheating.

At low values of superheating the interface was often slightly curved, with the curvature and advancing front changing somewhat in many cases. At higher values of superheating straight interfaces were observed, often at right angles to each other, though the interface might again swing around somewhat.

The even rate of advance of the interface was, however, not maintained in about one crystal in five when striations were observed to occur parallel to the advancing interface. The striations followed the advancing interface, the spacings differing in various crystals from 5 to 100 μ. More often than not the striations were parallel to the 'b' crystallographic axis, as was also found to be the case when $AgNO_3$ crystals were pressed between glass slides, producing slip lines.

The striations made the growth rates spasmodic in nature and reduced their speeds. The advancing interface would slow down, or even stop at low values of superheating, then advance again, leaving behind it a striation and so on, as if the accumulated stress during transformation slowed down the transition, then relieved itself by slip, making the interface advance again. The striations are shown in Fig. 1.

The presence of stresses in a crystal during a transformation was verified by X-rays; a Laue photograph of a transformed crystal showed considerable asterism (Fig. 2). Also crystals when examined several hours after a transformation were found to have developed cracks.

The presence of stresses was also borne out by the fact that if a transition started in the centre of the crystal it was usually slower by a factor of two or more until the growing phase reached the edge of the crystal, when the rates became normal. The very beginning of the phase change was also often slower; while the rates were somewhat faster when growing along an edge or towards a sharp corner.

The isothermal growth rates were constant with time in a given direction only and varied considerably when measured along different crystallographic directions. The rates measured were along the 'a' and 'b' axes of the orthorhombic crystals and these will now be discussed in the following section.

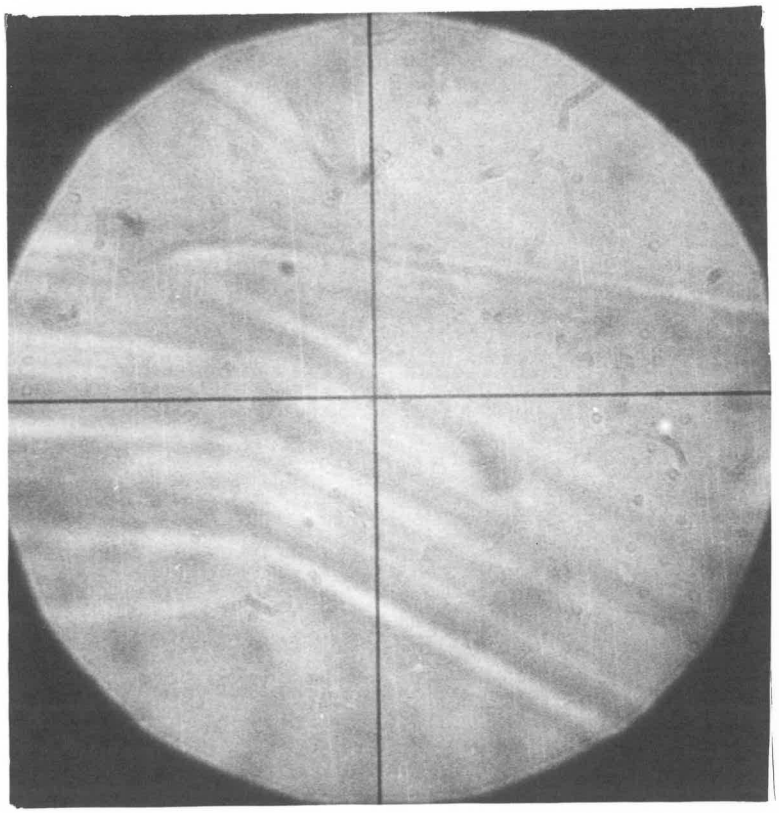

FIG. 1

$AgNO_3$ crystal showing striations after a phase transformation.

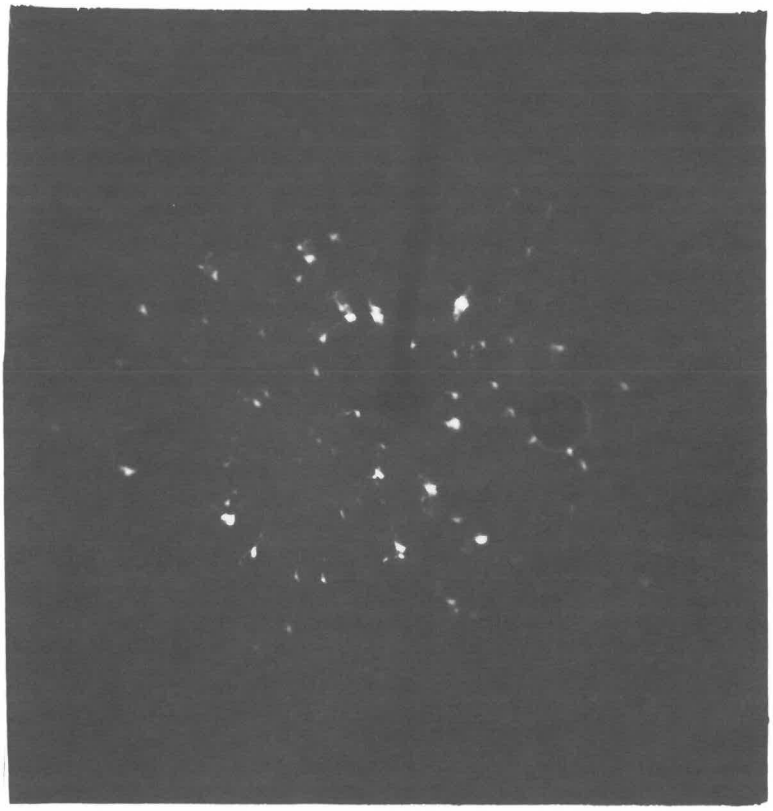

FIG. 2

An X-ray photograph showing asterism after a phase change.

(b) GROWTH RATES ALONG 'a' AND 'b' CRYSTALLOGRAPHIC DIRECTIONS

When the interface of the transforming crystal moves in the direction of the a-axis of the room temperature form crystal, the growth rate is said to be along the 'a' direction; similar notation is used for the 'b' direction.

The crystallographic axes of the orthorhombic crystals were found easily from the known morphology of the crystals used (001), with the aid of polarized light, and λ-compensating plate. But the orientations of the trigonal high temperature form crystals could not be determined, as the examination of crystals at high temperatures was difficult, and nothing was known about their morphology. Also a single orthorhombic crystal often changed to several crystallites of the trigonal phase, in quite a random fashion, there being no apparent correlation between the phases.

It was found that the relative growth rates along the 'a' and 'b' directions of the orthorhombic phase bore a definite relationship to each other, irrespective of the orientation, or number of crystallites, of the growing high temperature phase. The 'b' direction was found to be always faster than the 'a' direction in the ratio as three is to two. This was the average difference, however, and individual rates did vary somewhat, but the 'b' direction always remained the faster one, provided that the rates were measured on the same growing nucleus, if more than one were present. With different nuclei this relationship was a little less regular.

The fact that consistent results could be obtained along the directions of the parent phase suggests that it is this phase which is mainly responsible for the varying growth rates and not the forming high temperature phase. Typical growth rates along the two directions are shown in Fig. 3. Growth rates at different degrees of superheating will be discussed in the next section.

(c) GROWTH RATES AT DIFFERENT DEGREES OF SUPERHEATING

The growth rates observed rose exponentially with temperature, to about 0.52 mm./sec. at eleven degrees superheating. Visual observations showed that the rates kept on increasing at still higher temperatures. The rates along the b-axis of the room temperature form were always faster than the rates along the a-axis, and furthermore they kept their relative values, irrespective of the degree of superheating and the absolute growth rates observed.

A plot of growth rates against the temperature, for both the 'a' and 'b' directions, is shown in Fig. 4. The rates are seen to lie on two smooth curves, showing consistent growth rates. This picture is, however, spoiled somewhat if crystals which are slightly decomposed are included. Decomposed crystals did give rates which were sometimes double the normal rates or even higher. Different size crystals also showed varying rates and these will be discussed in the following section.

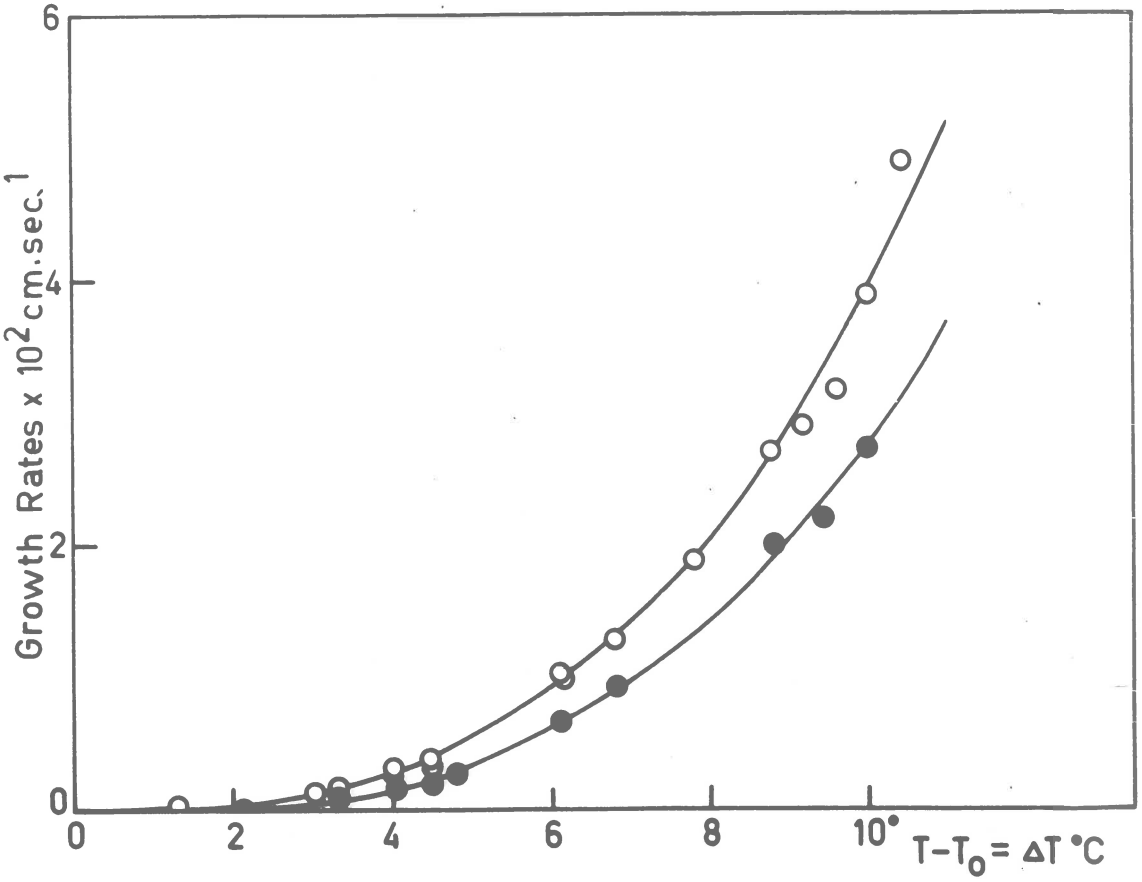

FIG. 4 Growth rates along the a and b axes plotted against the temperature ($T-T_o$ °C) on superheating.

(d) GROWTH RATES FOR DIFFERENT SIZE CRYSTALS

The growth rates described in the foregoing section referred to crystal plates of about 0.5 mm. across and 0.05 mm. thick. Growth rates on crystals smaller than these (about 0.15 mm. x 0.15 mm. x 0.03 mm.) were also measured and found to be slightly lower, though the rates were not always consistent, a few being even higher than those for the corresponding larger crystals.

Growth rates measured on larger crystals (1.3 mm. x 1.3 mm. x 0.07 mm.) were found to be bigger by almost 60%; though here again some inconsistency in results was obtained, possibly owing to insufficient number of crystals studied.

These observations show that even though the rates do vary to some extent from crystal to crystal, there exists a definite tendency for the larger crystals to have higher growth rates.

(e) GROWTH RATES IN CRYSTALS CONTAINING CONTROLLED AMOUNTS OF IMPURITIES

Two dozen $AgNO_3$ crystals, containing cadmium nitrate as a specially added impurity, with the cadmium to silver ratio varying from 0.075 to 0.225 atomic percent, were studied and their growth rates found to vary from normal to higher rates, up to about 75%. The average rate was about 20% higher. Growth rates on a few crystals containing lanthanum and strontium nitrates as impurities showed similar results.

Crystals containing foreign ions seem to have a slight tendency to higher rates, though it is not very pronounced, apparently less so than for slightly decomposed crystals.

2. GROWTH RATES IN WHISKERS

$AgNO_3$ whiskers were grown and their growth rates measured. Thin whiskers were found to be fragile on handling, being easily bent and their crystalline perfection impaired (the uniform interference colours under crossed Polars were upset). Perfect portions of whiskers, about 0.75 mm. long and 0.015 mm. diameter were selected and heated to the transition temperature. They nucelated at about the same degree of superheating as the crystal plates, but their isothermal growth rates were far less uniform, decreasing and then increasing again, or even stopping sometimes. A typical isothermal growth rate is shown in Fig. 5. The spasmodic rates occurred in thin whiskers only, thicker ones having much more uniform rates. As in crystal plates the whiskers changed to one or more crystallites. Their maximum growth rates were about normal or even higher, but the average rates were much lower, and somewhat inconsistent, owing to the spasmodic isothermal growth rates.

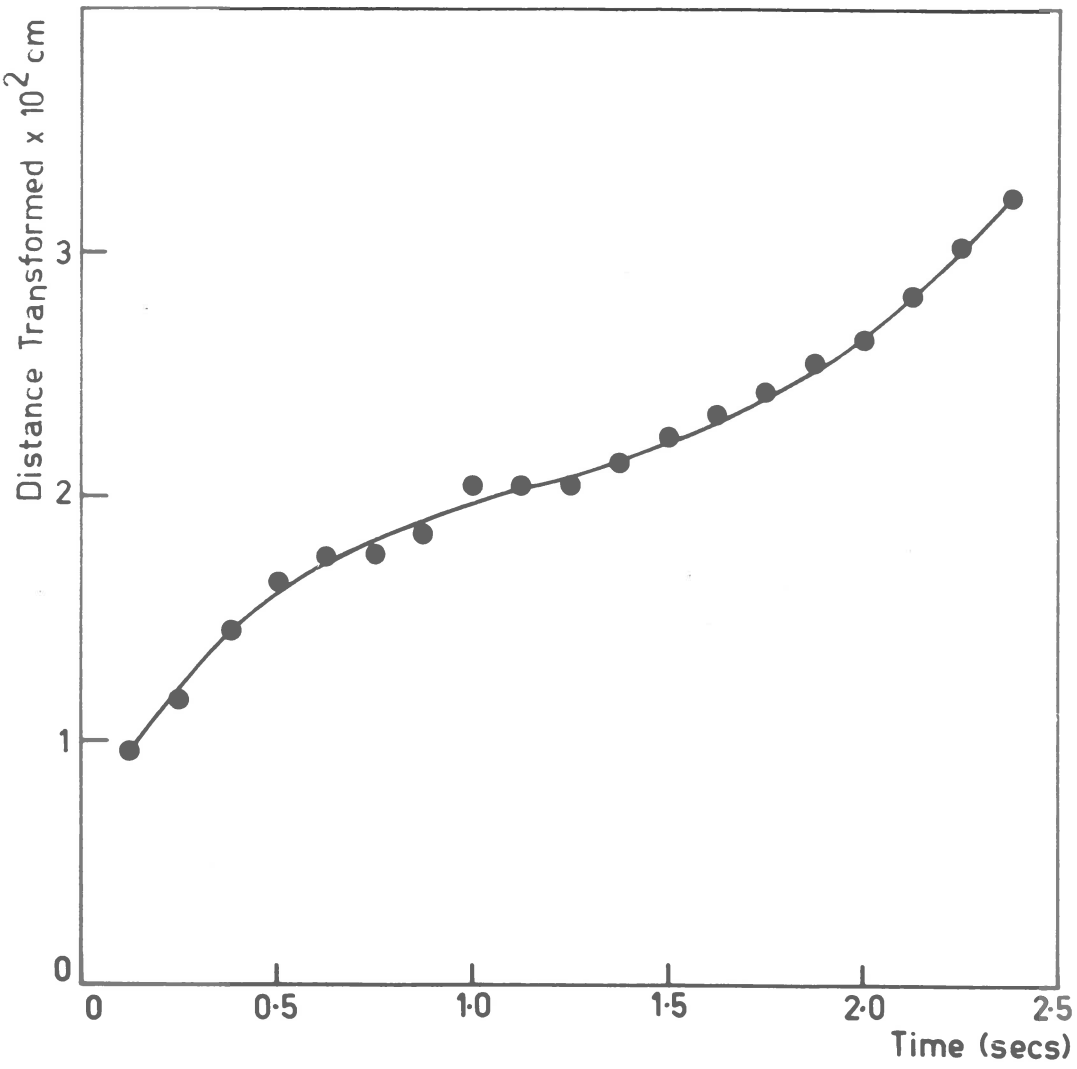

FIG. 5 Isothermal growth rates in $AgNO_3$ whisker on superheating.

PART B. $AgNO_3(I) \longrightarrow AgNO_3(II)$ TRANSITION

INTRODUCTION

The room temperature form $AgNO_3$ crystals which transformed to the trigonal high temperature form were left for ten minutes at 170°C. i.e. ten degrees above the transition temperature, to destroy any nuclei of the low temperature phase that may still have been present, and to anneal strains.

After this treatment the crystals were cooled rapidly to any temperature desired and nucleated artificially with a room temperature form crystal; there being no apparent relationship between the orientations of the crystals. The transformation was observed and recorded in the same manner as for superheating; the degree of supercooling varied from a few degrees to 190°C.

1. GROWTH RATES IN (001) PLATES

(a) ISOTHERMAL GROWTH RATES

The isothermal growth rates on supercooling displayed, on the whole, the same characteristics as the growth rates on superheating, with some small difference however. The interface on supercooling, for example, was sharp and smooth down to the temperature of 30°C., but below this temperature the interface was irregular and the crystal transformed to a mass of crystallites, as opposed to one or several crystallites at higher temperatures. The growth rates themselves were

constant with time, with again the slight increase in rates along an edge, or when moving towards a sharp corner, but the initially slower rates on superheating, at the start of the transition, were absent, possibly owing to the artificial nucleation which always initiated the transition at the edge of a crystal and not in the interior of it.

On superheating the growth rates slowed down or even stopped when the temperature was less than one degree above the transition temperature, but on supercooling this phenomenon was observed for up to four degrees below the transition point. Striations were also observed as often on supercooling as they were on superheating, a crystal often displaying them during both transformations. These striations again produced spasmodic growth rates as well as slowing the rates down.

As on superheating the isothermal growth rates were again dependent on direction, but they were not correlated with any crystallographic axes, as these were not known and often more than one crystallite was involved. The maximum growth rates were therefore measured and these correlated with growth rates at different temperatures.

When a high temperature form crystal was composed of several crystallites, the growth rate, as well as the interface of the growing room temperature form, did not change visibly when growing through different crystallites, or when crossing the intercrystalline boundary; but when the high temperature form consisted of only two crystallites,

elongated in the direction of growth, when small variations in rates could be more easily detected, the growth rates were indeed found to vary markedly in several instances. The growth rates differed by as much as 100% in the two crystallites, as well as displaying a retardation at the interface. It is thus apparent that on supercooling the orientation of the parent phase produces variable growth rates also, even though it may not be to the same extent as on superheating.

(b) GROWTH RATES AT DIFFERENT DEGREES OF SUPERCOOLING

As the temperature was reduced from the transition point the rates were found to increase almost linearly, except for the first few degrees, were the rise was parabolic and uncertain, until they reached a maximum value of 0.394 mm./sec. 58.5 degrees below transition temperature, then decreased with further fall of temperature, finally going asymptotically to zero at -30°C. (no growth was observed for one hour).

Individual rates at a given temperature did vary to some extent; the discrepancy being somewhat larger nearer the transition point temperature (160°C), and less pronounced further away from it. The maximum difference in growth rates, at a given temperature, could be as high as 100%. Therefore a large number of transformations had to be studied to yield accurate results. Slightly decomposed crystals again gave higher rates, particularly near the transition temperature (before maximum), and almost normal rates far away from the transition

temperature (after maximum). A graph giving the growth rates as a function of temperature is shown in Fig. 6.

(c) GROWTH RATES FOR DIFFERENT SIZE CRYSTALS

Crystals larger (about 1.3 mm. x 1.3 mm. x 0.07 mm.) and smaller (about 0.15 mm. x 0.15 mm. x 0.03 mm.) than those discussed in the foregoing section were studied and their growth rates measured in a temperature range of 100 deg. The larger crystals gave substantially higher rates, by about 60% on the average, while the smaller ones gave somewhat lower rates, by about 15%, than the intermediate size crystals discussed previously. Some overlapping of rates did occur, owing to scatter in rates, but it was evident, as on superheating, that larger crystals gave higher rates.

Growth rates for the large and small crystals as a function of temperature are given in Fig. 7.

(d) GROWTH RATES IN CRYSTALS CONTAINING CONTROLLED AMOUNTS OF IMPURITIES

After the $AgNO_3$ crystals, containing $Cd(NO_3)_2$ as an impurity, were transformed to the high temperature form, they were cooled and transformed back to the room temperature form, and their rates measured. These were found, as on superheating, to be almost identical with the pure $AgNO_3$ crystals with the rates being, in some cases, higher in the

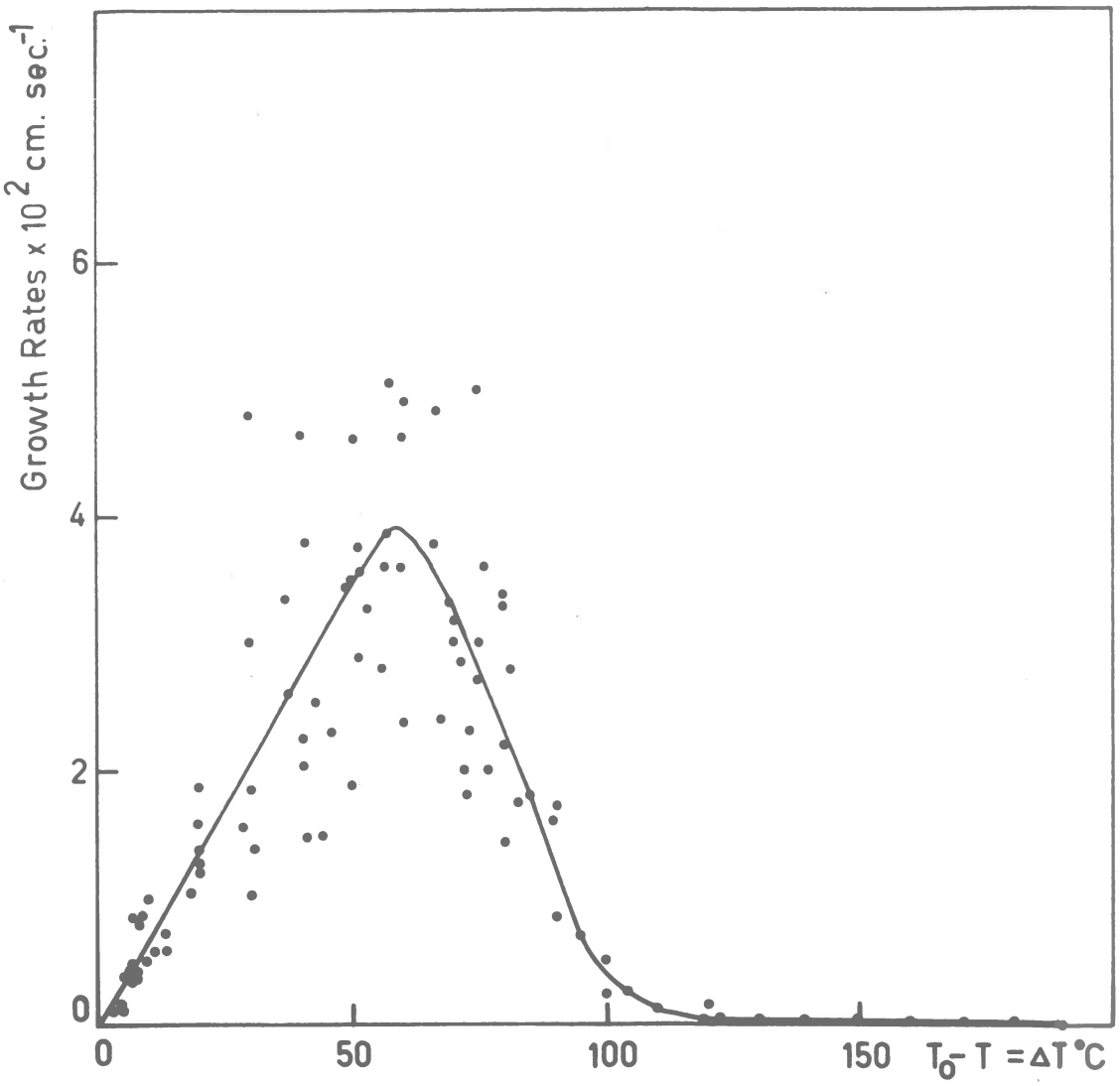

FIG.6 Plot of growth rates against temperature change (T_o-T = ΔT^{o}C) on supercooling.

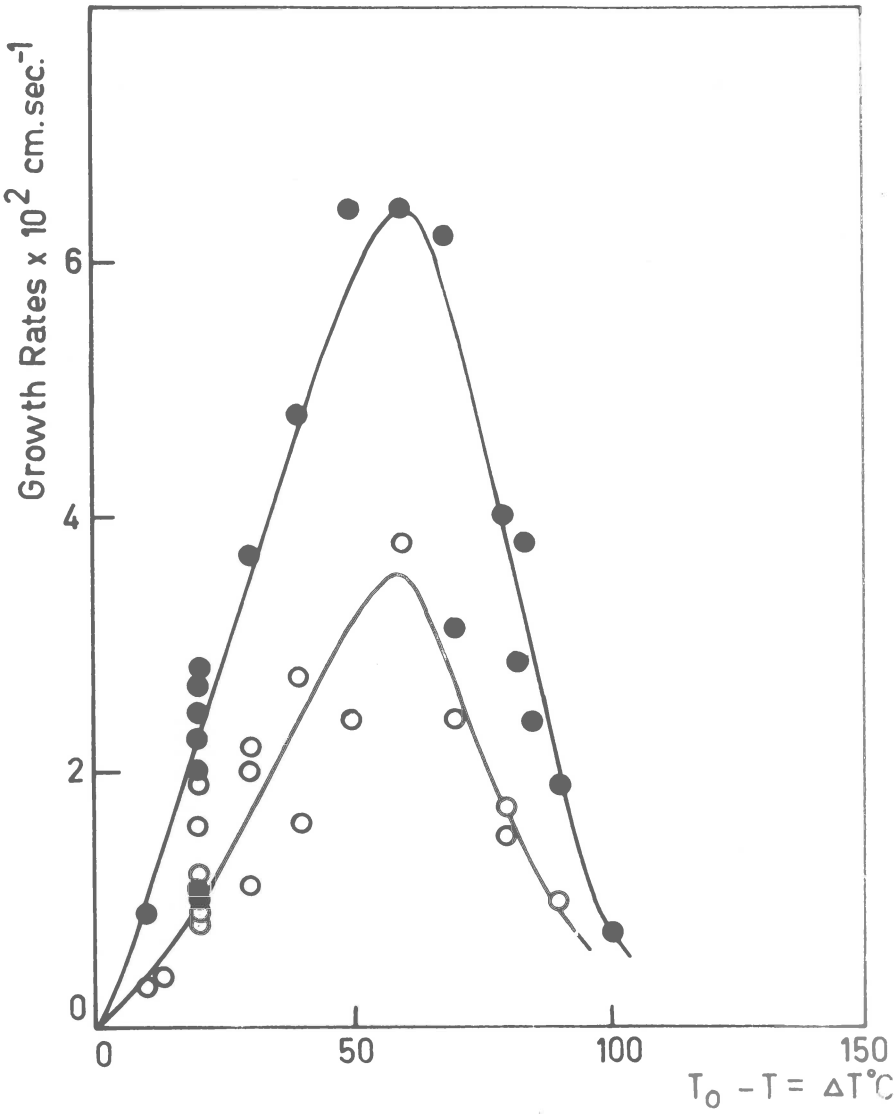

FIG.7 Plot of growth rates against temperature for different size crystals on supercooling.

temperature range close to the transition temperature i.e. before the maximum; after maximum normal growth rates were obtained. Here again it is evident that impurity ions have little effect on growth rates.

2. GROWTH RATES IN WHISKERS

The $AgNO_3$ whiskers, after being transformed to the high temperature form and annealed, were supercooled and transformed back to the room temperature form. They supercooled just as easily as ordinary crystals, and nucleated in the same way, but gave spasmodic isothermal growth rates, as on superheating, and instead of going to one or more crystallites of variable orientation, they almost always changed to a single crystal with the extinction along the cross-hairs of the microscope eye-piece i.e. back to the original orientation, or sometimes at 45 deg. to it. The whiskers were also seen, in a few cases, to bend during transition, a phenomenon not observed on superheating.

The maximum rates were comparable to the rates in crystal plates, but the average values were lower and less reproducible. The growth rates were measured in a temperature interval ranging from the transition temperature to room temperature, and they displayed the same variable rates with temperature as the crystal plates.

CHAPTER IV DISCUSSION OF RESULTS

PART A. $AgNO_3$ (II) ⟶ $AgNO_3$ (I) TRANSITION

1. CALCULATION OF ACTIVATION ENERGY USING TURNBULL'S EQUATION

The growth rates of the orthorhombic to the trigonal phase transformation were measured in a temperature range of eleven degrees; hence using any of the rate equations derived in Chapter I the activation energy for this phase transition can be found. Turnbull's equation was used, as it is more general and its pre-exponential can be evaluated more readily.

Turnbull's equation (38)

$$v = \sqrt{\lambda}\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(-\frac{\Delta H_a}{RT}\right)\left[1 - \exp\left(\frac{\Delta G}{RT}\right)\right]$$

gives after taking logarithms and rearranging

$$\log v - \log(1 - \exp(\Delta G/RT)) = \log\left(\sqrt{\lambda}\exp\frac{\Delta S_a}{R}\right) - \frac{\Delta H_a}{2.3RT} \qquad (40)$$

from which by plotting $\log v - \log(1 - \exp(\Delta G/RT))$ against $1/T$ the energy of activation (ΔH_a) and the pre-exponential $\sqrt{\lambda}\exp\left(\frac{\Delta S_a}{R}\right)$ can be found.

Before doing this, however, the values of the free energy difference between the phases (ΔG), at various temperatures, had to be known. These had to be calculated from the known heat capacity data (C_p), for the two phases, and the known entropy (ΔS) and enthalpy (ΔH) change for the transition.

The C_p curve for the orthorhombic room temperature phase, from zero to 300 deg. absolute, was obtained from Smith, Brown and Pitzer,[34] and from 300 deg. to the transition temperature, from Kelley;[35] the ΔC_p for the transition (1.4 cal./deg./mole) was also obtained from Kelley, as was the value of C_p for the trigonal high temperature phase. The C_p curves in the unstable regions, not given in literature, were extrapolated from the known values, keeping in mind the ΔC_p value and the ΔH and ΔS values for the $AgNO_3$ transition. The ΔH value chosen was 660 cal./mole, and the ΔS value 1.52 cal./degree/mole, as given in the National Bureau of Standards Thermodynamic Tables.[36] These are about the average values, other values quoted in the literature varied by almost ± 20% e.g. from 544 to 784 cal./mole for ΔH.

The C_p curves were plotted against absolute temperature, to obtain the ΔH values, and the logarithms of absolute temperature, to get the ΔS values at different temperatures. As, however, the absolute values of ΔH and ΔS could not be determined, owing to the lack of precise C_p data in the regions were the two phases are unstable, as well as the ΔH not being zero at zero absolute temperature, the values of ΔH and ΔS were calculated from the graphs, counting from the equilibrium values at the transition point, and these figures were then added to the equilibrium values. Since by definition $\Delta G = \Delta H - T\Delta S$, the required ΔG values were thus obtained.

Knowing now the ΔG values for all the temperatures required, $\log v - \log(1 - \exp(\Delta G/RT))$ was plotted against $1/T$, and ΔH_a and

$\sqrt{\lambda}\exp(\frac{\Delta S_a}{R})$ obtained. This plot is shown in Fig. 8. As is evident from the graph the activation energy does not have a constant value, but decreases with increasing temperature, from 276 kcal./mole, to 86 kcal./mole; the corresponding pre-exponentials being 5×10^{134} to 2.7×10^{42}. The plot shows the rates along the b-direction only, the a-direction yields similar ΔH_a's, but slightly lower pre-exponentials.

2. COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL RATES

According to the absolute reaction rate theory the standard free energy of activation for any reaction should be constant. But the experimental results yield an activation energy value which changes smoothly with temperature, being very high at first, but decreasing rapidly and going possibly to a reasonable finite value at still higher temperatures.

This is a puzzling picture which can only be explained as due to a changing mechanism, or more than one molecule jumping across the interface at once, or the molecules bouncing back, or some such effects. The simple theory is, however, unable to account for it. Another puzzling factor is that $AgNO_3$ transition is not an isolated case, which disagrees with the rate equations, but that this decreasing activation energy is a rather common occurrance observed by Müller,[25] in the recrystallisation of rock salt, and by various other workers, in the recrystallisation of metals, as given by Burke and Turnbull.[20]

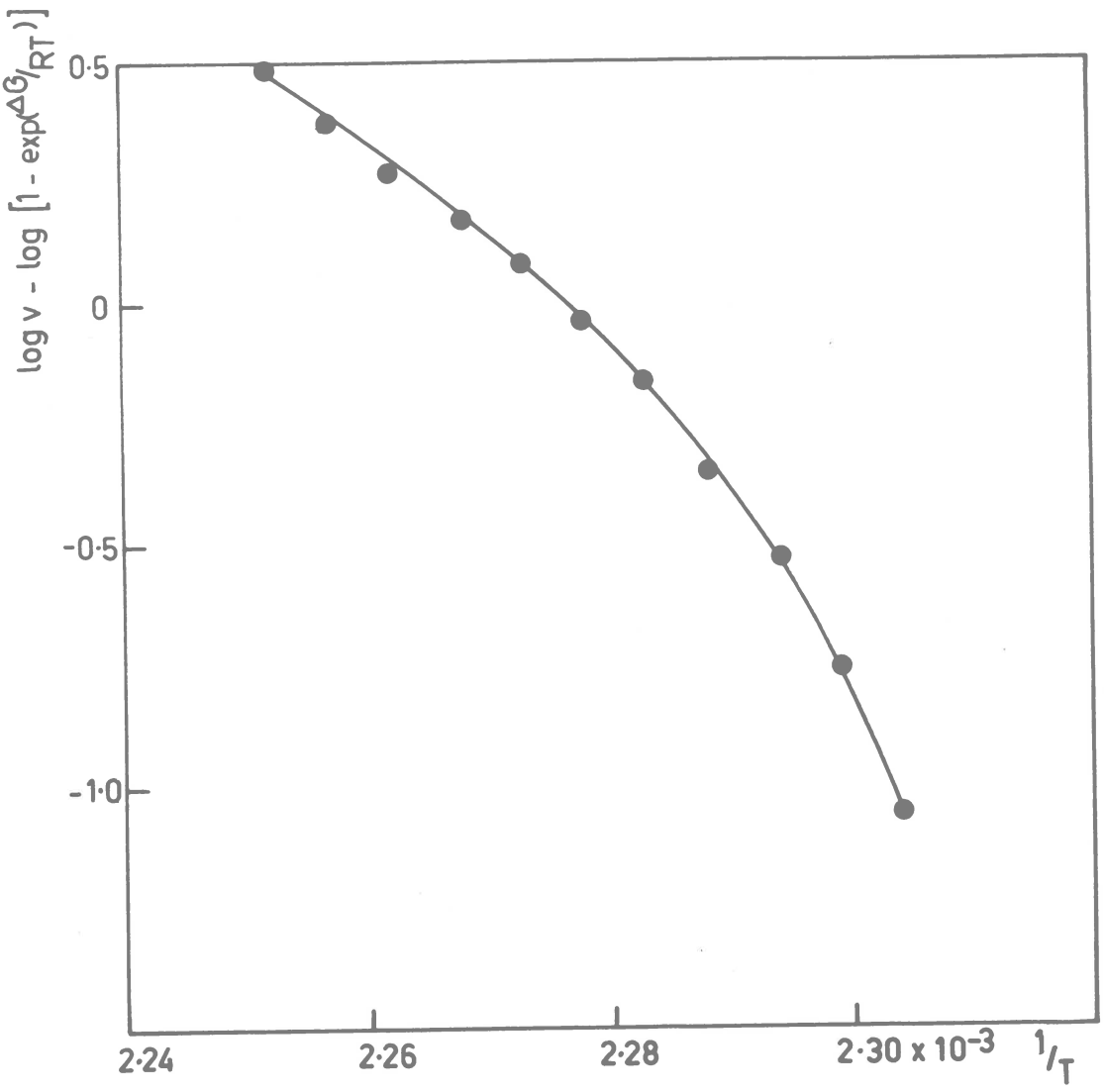

FIG.8 Plot of log v - log $[1-\exp(\frac{\Delta G}{RT})]$ against 1/T on superheating.

Thus the theory and experimental results are at variance and some further explanation is required.

The pre-exponential factor according to Turnbull's equation should be $\sqrt{}\lambda\exp(\frac{\Delta S_a}{R})$, or taking $\sqrt{} = 5 \times 10^{12}$, $\lambda = 5 \times 10^{-8}$ cm. and $\exp(\frac{\Delta S_a}{R}) = 6.9 \times 10^{6}$, if $\Delta S_a = 31.5$ cal./deg./mole, then $\sqrt{}\lambda\exp(\frac{\Delta S_a}{R})$ should be about 1.7×10^{12}. The experimentally obtained values are from roughly 10^{42} to 10^{134}, or vastly greater than theoretically predicted. But it must be remembered that the activation energy values are also much greater than normally expected, and since these occur in the negative exponential they would tend to make the overall rates, as given by the equation, not as vastly greater as the pre-exponentials might indicate. Taking Turnbull's equation

$$v = \sqrt{}\lambda\exp(\frac{\Delta S_a}{R})\exp(-\Delta H_a/RT)(1 - \exp(\Delta G/RT))$$

where $\Delta H_a = 24{,}000$ cal./mole $\exp(\frac{\Delta S_a}{R}) = 1.7 \times 10^{12}$

$T = 438^{\circ}K$ $\Delta G = -7.35$ cal./mole

we get $v = 1.8 \times 10^{-2}$ cm./sec. But the experimentally obtained value is $v = 5.7 \times 10^{-3}$ cm./sec., which means that the experimental rates are only about three times slower than the theoretically predicted rates.

This means that the growth rates are roughly of the right order, even though the activation energy, and the pre-exponential, are far too high.

3. COMPARISON WITH OTHER RATE EQUATIONS

Other equations derived in Chapter I besides the Turnbull's equation used, were Hartshorne's equation (equation 20), which is essentially similar to Turnbull's equation, and which yields the same results, with the difference that the activation energy obtained would be called the heat of sublimation of the unstable phase, and the pre-exponential, worked out theoretically, would have a somewhat lower value. The rates obtained would be too high for his equation, as found by Hartshorne himself e.g. sulphur transition, and nothing new would be gained by applying it, but the additional fact that the activated state was equivalent to the heat of sublimation of the unstable phase.

Dunning's equation (equation 24) is somewhat different, the rate of growth being based on the rate of two dimensional nucleation of the stable phase on a flat surface, but it too was found to be incompatible with the experimental results.

Bradley's equation (equation 30) is again essentially similar to Hartshorne's and Turnbull's equations and the same values for the activation energy and the pre-exponential would be obtained.

Mott's 'island model' equation (equation 39) is of a different form, it assumes n molecules of the unstable phase to melt and move across the interface to the stable phase.

In Mott's equation the same log v - log $(1-\exp(\Delta G/RT))$ is plotted against $1/T$, and the same values are obtained for the activation energy and the pre-exponential; but the activation energy is now equal to nL, where n is the number of molecules which melt in the activated process and are simultaneously tranferred across the interface to the stable phase, and L is the latent heat of fusion of the unstable phase. The pre-exponential consists of $\sqrt{\lambda}\exp(nL/RT_m)$, where T_m is the melting temperature. Since L is known, we can calculate n, assuming the mechanism to apply. The pre-exponential has now a new term in it, viz. $\exp(nL/RT_m)$, a term bigger than $\exp(\frac{\Delta S_a}{R})$, therefore the overall pre-exponential should now be greater, as is in fact observed experimentally. The variable activation energy may be interpreted as the variation in n, with n decreasing as the melting temperature is approached; n varying from 83 to 26. The experimentally observed pre-exponentials are now in a better agreement with the theoretical ones; the theoretical varying from 3.7×10^{128} to 3.2×10^{43}, and the experimental from 5×10^{134} to 2.7×10^{42}, using $\sqrt{\lambda} = 10^5$, and the full Mott's pre-exponential $\sqrt{\lambda}\exp(nL/RT_m)$. Thus it is seen that Mott's 'island model' equation does give a better agreement between theoretical and experimental results, further away from the transition temperature, but still poor agreement near the transition temperature.

4. MODIFIED RATE EQUATION INCORPORATING STRESSES

The presence of striations, cracking of the crystals, and asterism in X-ray photographs after a transition all prove conclusively that considerable stresses occur during a phase transformation, and that an appreciable strain energy must be present to oppose the transition. This real strain energy is not included in any of the theoretical equations discussed so far, where the driving force for the phase change was assumed to be the volume chemical free energy difference (ΔG_v) between the phases, without any contribution from other forms of energy. If, however, the strain energy is included, as an additional force influencing the transition, then Turnbull's equation, derived in the same way as in Chapter I, but with the difference that the atoms now posses an additional strain energy, becomes

$$v = \sqrt{\lambda} \exp\left(\frac{-\Delta G_a + G_s \text{ (unstable)}}{RT}\right) \left[1 - \exp\left(\frac{\Delta G_v + \Delta G_s}{RT}\right)\right] \quad (41)$$

where G_s (unstable) is the strain energy of the unstable phase, and ΔG_s is the strain energy difference between the phases. Or omitting G_s (unstable), as it is small compared with ΔG_a, equation (41) becomes

$$v = \sqrt{\lambda} \exp\left(-\frac{\Delta G_a}{RT}\right) \left[1 - \exp\left(\frac{\Delta G_v + \Delta G_s}{RT}\right)\right] \quad (42)$$

or

$$v = \sqrt{\lambda}\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(\frac{-\Delta H_a}{RT}\right)\left[1 - \exp\left(\frac{\Delta G_v + \Delta G_s}{RT}\right)\right] \qquad (43)$$

From equation (43) a single valued activation energy can be obtained, as shown in Fig. 9. The value of ΔH_a is 147 kcal./mole, and the pre-exponential is 1.14×10^{69}.

The strain energy is assumed to oppose the transformation, as witnessed by the slowing down of the growth rate, at low values of superheating, and just before a striation occurs, This strain energy term is itself the sum of two terms; one a constant, corresponding to the strain produced during a phase change, owing to different specific volumes of the two phases, and the other a variable term, proportional to the rate of transformation; a faster rate preventing the annealing of strains and thus increasing the strain energy term. The overall strain energy is of the form

$$\Delta G_s = a + bv \text{ cal./mole}$$

where $a = 1$, and $b = 2 \times 10^2$

v being the growth rate in cm./sec.

At eleven degrees superheating ($\Delta T = 11^\circ$) $\Delta G_s = 11.4$ cal./mole, when $\Delta G_v = 16.15$ cal./mole. The strain energy can thus exert a considerable influence on the growth rates.

This new equation, besides incorporating a term which undoubtedly plays an important role in the kinetics of phase transitions, gives a

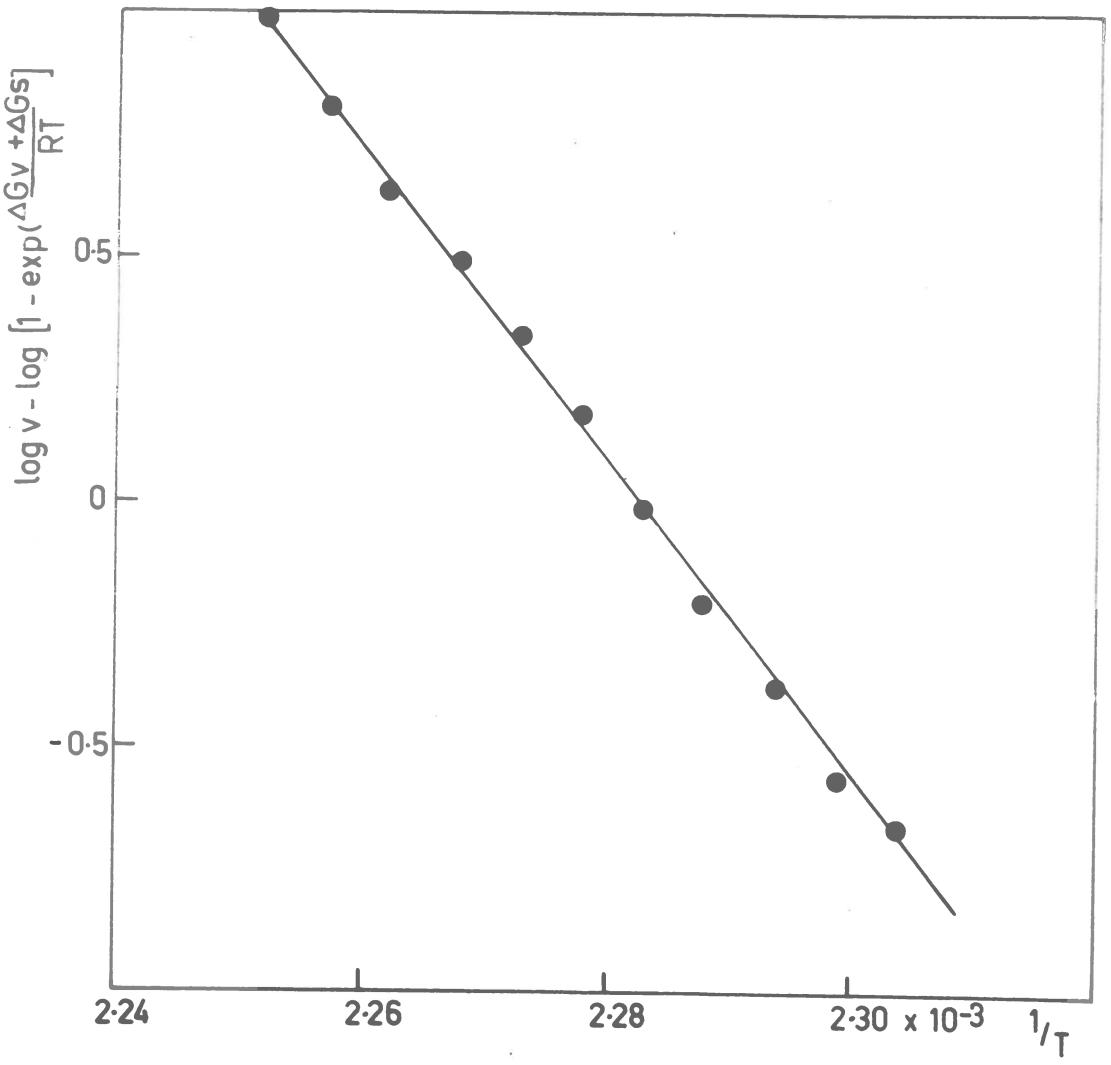

FIG.9 Plot of log v - log[1 - exp($\frac{\Delta Gv + \Delta Gs}{RT}$) against 1/T on superheating.

single valued activation energy term, even though it is very high; the pre-exponential is likewise too high to have any real meaning.

When ΔG_s is added to Mott's 'island model' equation, n, the number of molecules moving across, is 44, and the pre-exponential is 3.4×10^{70}, where $\exp(nL/RT_m)$ is 3.4×10^{65}, which is in close agreement with the experimentally observed value.

This equation, incorporating a strain energy, thus possesses some additional merits which the ordinary equations do not have, though again it is not quite in quantitative agreement with the experimental results.

PART B. $AgNO_3$ (I) ⟶ $AgNO_3$ (II) TRANSITION

1. CALCULATION OF ACTIVATION ENERGY USING TURNBULL'S EQUATION

Growth rates on supercooling were obtained in a temperature range of 190 deg.. This large range of temperatures permitted an accurate evaluation of the activation energy for this phase transition, using Turnbull's equation (equation 38), as on superheating.

By plotting $\log v - \log(1 - \exp(\Delta G/RT))$ against $1/T$, and using the calculated values of ΔG, obtained in the same way as for superheating, with the only difference that the H and S values read off from the C_p curves were subtracted from the ΔH and ΔS values for the transition and not added to them. Values for the activation energy and the pre-exponential were thus obtained, as shown in Fig. 10. It is evident from this graph, that not one but two activation energy terms are obtained: one of 21.1 kcal./mole, at low temperatures, far removed from the transition point, were the growth rates decrease with decreasing temperatures, or after the maximum in rates has been passed; and a slightly negative activation energy near the transition point, before the maximum in growth rates is reached, i.e. in the temperature range were the rates increase with decreasing temperatures. The pre-exponential corresponding to the activation energy of 21.1 kcal./mole is 1.7×10^{12} cm./sec.

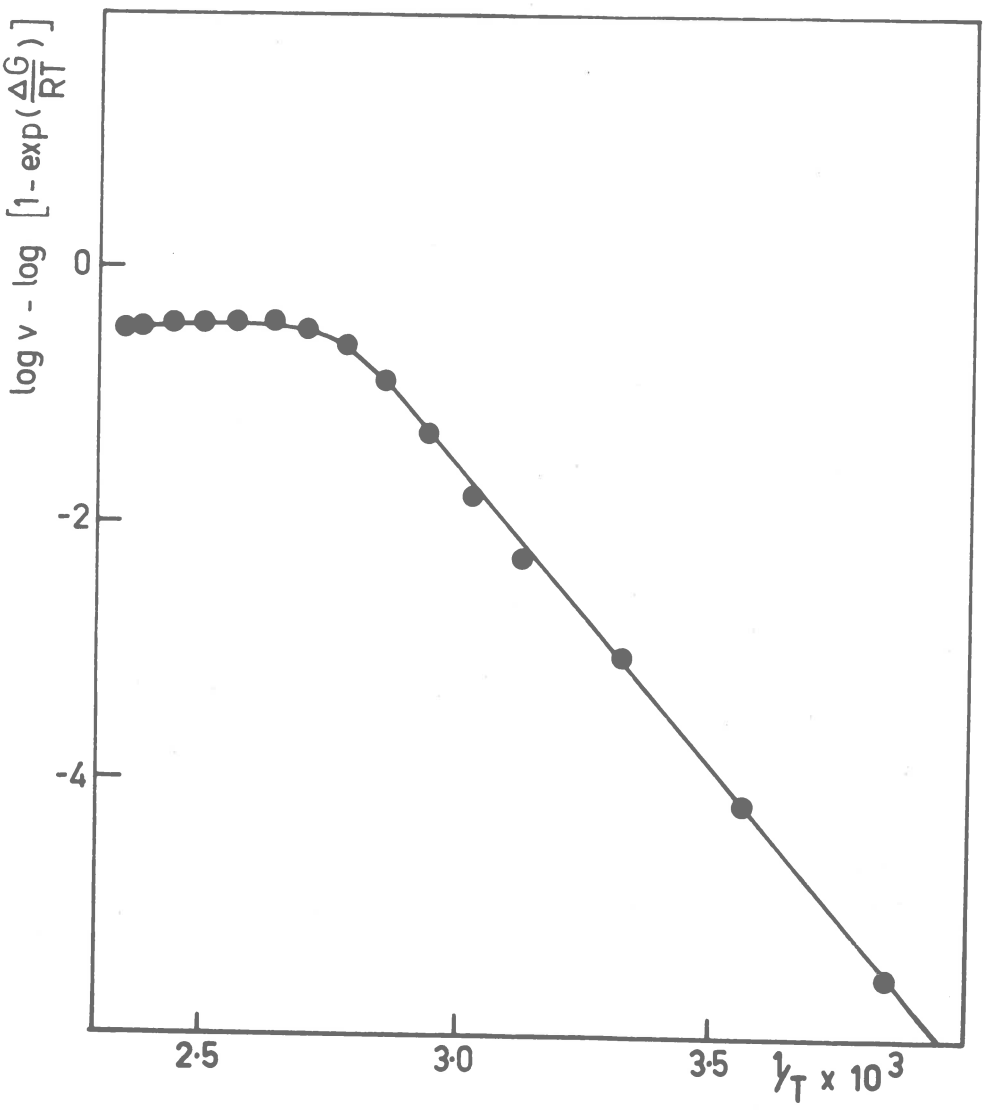

FIG.10 Plot of log v - log [1 - exp ($\frac{\Delta G}{RT}$)] against 1/T on supercooling.

The change of the activation energy to negative values points to the inapplicability of Turnbull's equation to this phase change, near the transition point (before maximum), possibly owing to a changing mechanism, or to some controlling factor or factors not considered by this equation. This incompatibility of this rate equation with experimental results, however, is not an isolated case, Hartshorne[4] obtained about the same results for the $\beta \rightarrow \alpha$ sulphur transition, as well as Eyring[37] for the formation of ice from super-saturated water vapour seeded with AgI crystals.

2. COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL RATES

Assuming that the rate equation does not apply near the transition point, since a negative activation energy has no physical significance, and assuming, as Hartshorne did,[8] that the activation energy far removed from the transition point, is the true representive activation energy for the mechanism assumed, the activation energy is then 21.1 kcal./mole, a value which is of the right order, for the heats of sublimation possessed by similar substances, e.g. S = 23 kcal./mole and HgI_2 = 19 kcal./mole, though for $AgNO_3$ the heat of sublimation cannot be obtained since $AgNO_3$ decomposes before it reaches the temperatures of evaporation. The value of 21.1 kcal./mole is also comparable with the activation energy for grain boundary diffusion for metals, which is usually around 20 kcal./mole e.g. 20.2 kcal./mole

for silver.[38] The pre-exponential is 1.7×10^{12}, which should correspond with $\sqrt{}\lambda\exp(\Delta S_a/R)$.

Taking $\sqrt{} = 5 \times 10^{12}$, $\lambda = 5 \times 10^{-8}$ cm., and $\exp(\Delta S_a/R) = 3.3 \times 10^{6}$, if $\Delta S_a = 30$ cal./deg./mole,

then $\sqrt{}\lambda\exp(\Delta S_a/R) = 8.3 \times 10^{11}$

which means that the experimental rates are only twice the theoretical rates, or in very good agreement indeed, assuming that the entropy of activation ($\Delta S_a = 30$ cal./deg./mole) is not excessive.

3. COMPARISON WITH OTHER RATE EQUATIONS

Hartshorne,[4] as already mentioned, obtained essentially similar results for the $\beta \longrightarrow a$ sulphur transition (activation energy 22 $\longrightarrow$ 23 kcal./mole and the pre-exponential 5×10^{12} at low temperature). He assumed the activation energy to be equal to the heat of sublimation of the unstable phase (activated state identical with the vapour phase), the growth rates being equal to the rates of sublimation of the unstable phase into a vacuum. The experimental rates, far away from the transition point, were, however, too fast, by a factor of 10^3, when compared with the rates for sublimation. Near the transition point the rates were in better agreement with the calculated ones, but the activation energy was then negative. Hartshorne explained the anomalies in the activation energy and the rates as due to the molecules of the unstable phase not adhering to the stable phase, but bouncing back

near the transition point, i.e. the reverse reaction was appreciable, and hence the rates were slower and the activation energy negative, or not rate controlling.

Hartshorne[5] also tried the mechanism of phase growth on screw dislocation, as suggested by Frank,[15] where, at low values of supersaturation, near the transition point, the growth rates are proportional to the square of the supersaturation, or to $(1 - \exp(\Delta G/RT))^2$, and at temperatures removed from the transition point, the growth rates are proportional to the first power of the supersaturation, or to $(1 - \exp(\Delta G/RT))$. Hartshorne found the square law to apply near the transition point, for a few degrees only, and the linear law far away from the transition point; but for intermediate temperatures the power instead of changing smoothly from two to one, went to higher values (four to five in the $\beta \longrightarrow \alpha$ sulphur case). The $AgNO_3$ transtion showed similar results, with the power reaching even higher values than in the case of the sulphur transition.

Dunning's equation, where the growth rates are governed by two dimensional nucleation, was tried by plotting $\ln v - E/RT$ against $1/(T(T_o - T))$, but a smooth curve, instead of a straight line was obtained, especially near the transition point, so that this equation again did not represent the experimental facts to any greater advantage than the previous ones.

Bradley's equation is based on the same assumptions as Hartshorne's viz. vapour intermediate state, and evaporation into

a vacuum, and hence the $AgNO_3$ growth rates were similarly too high for this mechanism (high pre-exponential, though correct activation energy far away from the transition point.)

Turnbull's equation gives about the right pre-exponential, but it produces, as all the other equations do, a negative activation energy near the transition point.

Mott's 'island model' equation postulates n molecules melting at once and being transferred simultaneously to the stable phase. The experimentally obtained activation energy $\Delta H = 21.1$ kcal./mole, which is equivalent to nL, where L is the latent heat of fusion of the unstable phase ($L = 2.76$ kcal./mole obtained from Standard Thermodynamic Tables[36]). This makes n about 8, or Mott's equation postulates 8 molecules melting simultaneously and moving across to the stable phase. The pre-exponential $\sqrt{\lambda}\exp(nL/kT_m) = 7 \times 10^{14}$, which is higher than the experimentally obtained value of 1.7×10^{12}, i.e. experimental rates are slower than Mott's equation predicts by more than four hundred times, or in very poor agreement.

Eyring[37] applied another equation to the rate of growth of ice from supersaturated water vapour, but this equation unfortunately, as Eyring found out himself, yields an even bigger negative activation energy, though the same positive activation energy (21 kcal./mole) as all the other equations.

4. MODIFIED RATE EQUATION INCORPORATING STRESSES

As is evident from the previous section, none of the existing equations explain the mechanism of a phase transition fully: they all give negative activation energies near the transition point, when the growth rates increase with decreasing temperature, and they also fail to give a quantitative agreement between the theoretical and experimental results, except perhaps Turnbull's equation. Though again if we assume the growth rates to be of the right order, far away from the transition point, then the rates near the transition are too slow, if the values for the activation energy and the pre-exponential far away from the transition point are retained, and applied near the transition temperature. It must, however, be remembered that all the equations mentioned neglect the volume change occurring during a phase transition and thus stresses developed with a resulting strain energy. The presence of stresses in metallic transitions is a common occurrence, unequivocally proved for tin transition by Wolfson, Fine, and Ewald.[39] Stresses are, however, no less real, though perhaps not quite as large, in non-metallic transformations e.g. Hartshorne found cracks in transforming sulphur, even before the approaching interface, which indicates the presence of stresses not only at the interface, but also at some distance from it.[4]

$AgNO_3$ transition, as mentioned for superheating, also proved the existence of a considerable amount of stress during transformation, as

shown by X-ray photographs, cracks developing after transformation, and the appearance of striations during the transition. (The presence of cracks after a transformation was first discovered by Kennedy.[40]) The fact that striations are produced by pressure was proved by pressing $AgNO_3$ crystals between glass slides, under a microscope, and watching the striations appear. At first they appeared widely spaced and parallel to the b-axis of the crystal used, then more closely spaced and later parallel to the a-axis as well. The striations produced by pressure were accompanied by the cracking of the crystal; the pressure required to produce these striations was about 5×10^4 g./cm^2 obtained by placing known weights on a crystal of known surface area. Striations were produced both on superheating and on supercooling, but the bending of whiskers was only observed on supercooling, and the slowing down or stopping of growth rates occurred at temperatures further removed from the transition point on supercooling than on superheating.

The stresses developed oppose the transformation, producing both elastic and non-elastic strain. The elastic strain changes the transition point, as worked out by Honda and Sato;[41] the temperature shift (ΔT) being

$$\Delta T = \frac{0.355KT\left(\frac{\Delta V}{V}\right)^2}{\rho\lambda}$$

for a spherical sample, when one phase encloses the other completely,

K = Bulk Modulus of elasticity

$\frac{\Delta v}{v}$ = volume change per unit volume

T = transition temperature

ρ = density

λ = latent heat of transition,

which for supercooling works out to be about 7.8 deg.

when $K = 2.7 \times 10^5$ kg./cm.^{2}

$T = 433$ deg.K

$\Delta v/v = 0.0025 + 4.3$ cm.^{3}/cm.^{3}

$\rho = 4.3$ gm./cm.^{3}

$\lambda = 1.44 \times 10^2$ kg. cm./gm.

But for $AgNO_3$ transition, where thin crystal plates are used, one phase does not enclose the other, so that instead of the Bulk Modulus the Shear Modulus should be used. And since the Shear Modulus is usually about 1/3 to 1/2 the Bulk Modulus, the temperature shift (ΔT) should not be 7.8 deg., as worked out previously, but only 3 to 4 deg., as is in fact observed experimentally i.e. the transformation stops when ΔT is less than 4 deg.

The non-elastic or plastic strain produces a strain energy in both crystals, but since the orthorhombic room temperature phase is more compressible than the trigonal high temperature phase, it will be more strained, and hence possess a higher plastic strain energy.

This strain energy (ΔG_s) is positive and opposes the transformation in the case of $AgNO_3$ transition. Therefore ΔG_v (the chemical free energy), which is the driving force, is lowered so that smaller growth rates should result.

The new growth rate equation which considers not only the chemical free energy as the driving force in a phase transition, but includes the strain energy as well, can be derived in the same way as Turnbull's equation, with the only difference that the atoms now possess an additional strain energy, as well as a chemical free energy. This gives the same equation as derived for superheating,

$$v = \sqrt{\lambda} \exp\left(\frac{-\Delta G_a + G_s\,(\text{unstable})}{RT}\right)\left[1 - \exp\left(\frac{\Delta G_v + \Delta G_s}{RT}\right)\right] \qquad (41)$$

and simplifying again, since $\Delta G_a \gg G_s$ (unstable) and $\Delta G_a = \Delta H_a - T\Delta S_a$ we obtain

$$v = \sqrt{\lambda} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right)\left(1 - \exp\left(\frac{\Delta G_v + \Delta G_s}{RT}\right)\right) \qquad (43)$$

The strain energy (ΔG_s) is again, as on superheating, a sum of two terms: one a constant 'a', corresponding to the shift of the transition point (4 cal./mole), and the other a variable term 'b', proportional to the growth rate (v), and corresponding to the greater accumulation of stresses in a faster transition, and hence a build up of strain energy. Therefore

$$\Delta G_s = a + bv$$

where $a = 4$ cal./mole

$b = 1.85 \times 10^3$

v = growth rate in cm./sec.

The maximum strain energy is 76.5 cal./mole, the corresponding chemical free energy is 90 cal./mole. This occurs when the growth rates are at the maximum. Passed the maximum the strain energy decreases, while the chemical free energy keeps on increasing, and therefore the strain energy becomes less and less important, until at temperatures far removed from the transition point it becomes insignificant. Therefore it is only near the transition point (before maximum) that the strain energy is important, altering the growth rates appreciably, the region where all the anomalies in activation energy and growth rates occur.

Taking logarithms of equation (43) and plotting $\log v - \log (1 - \exp(\frac{\Delta G_v + \Delta G_s}{RT})$ against $1/T$, a single valued activation energy can be obtained throughout the whole temperature range, right up to the transition point. The same numerical value of 21.1 kcal./mole for the activation energy, and the same pre-exponential of 1.7×10^{12}, as in the unmodified Turnbull's equation, is obtained. This new plot is shown in Fig. 11. The new equation thus solves all the anomalies that all the other equations were at a loss to explain.

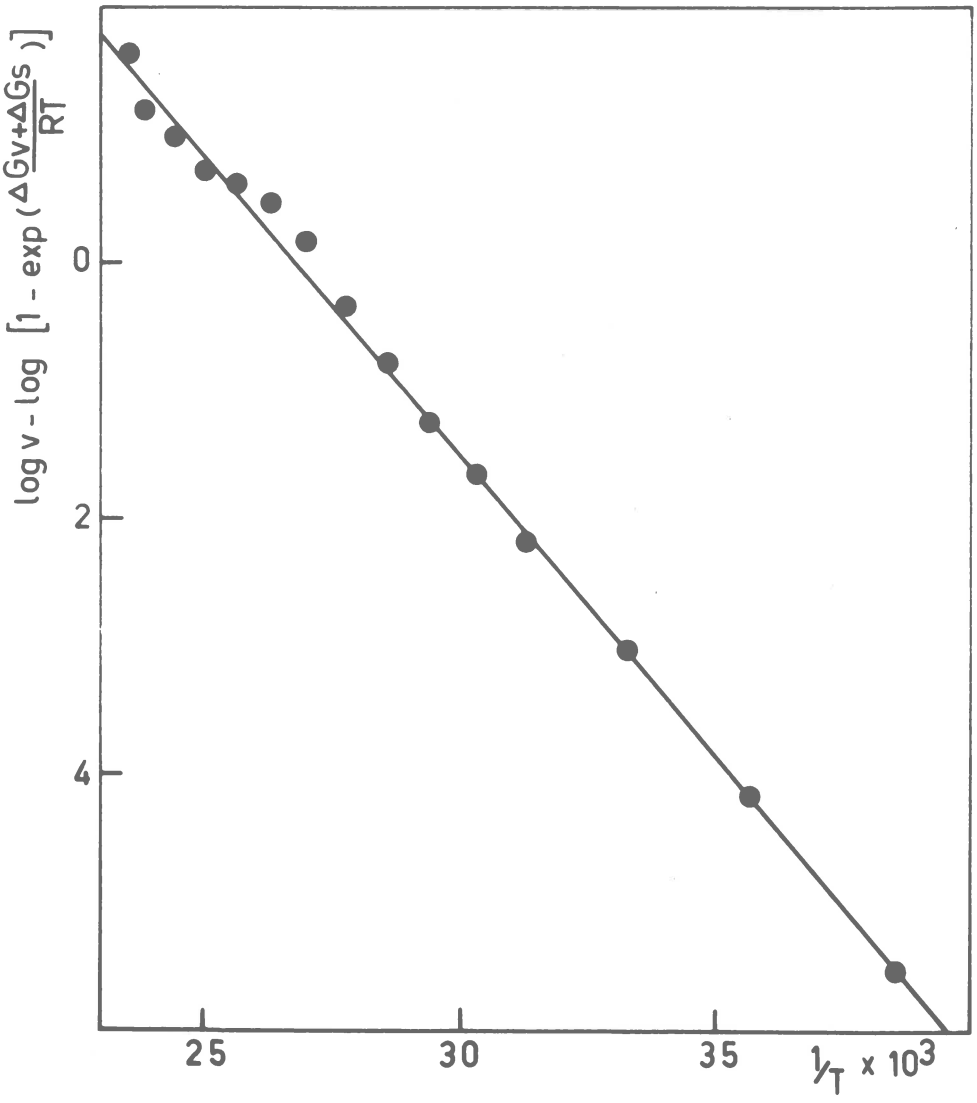

FIG.11 Plot of log v - log [1 - exp ($\frac{\Delta Gv + \Delta Gs}{RT}$)] against 1/T on supercooling.

It is seen from the graph, that the points corresponding to the activation energy near the transition temperature do not really lie on a straight line. Small changes in the growth rates, however, would result in a much better fit, changes which would be quite justifiable, since the growth rates are subject to a considerable scatter. Near the transition point the ΔG_v values are as yet quite small, though rising steadily, and the growth rates are also rising, so that the resultant driving force, which is the difference between ΔG_v and ΔG_s is small, and hence any slight changes in either ΔG_v or ΔG_s will produce large differences in growth rates. The activation energy can therefore quite easily be made into a perfectly straight line.

Higher growth rates were observed in the region near the transition point, 100% or more, when slightly decomposed crystals were used, or ones containing added impurities, at low temperatures normal growth rates were followed. This phenomenon, as well as slower rates than predicted by Turnbull's equation near the transition point, can be explained by the presence of this strain energy which opposes the transition, and possesses more weight near the transition point than far away from it. A change in the strain energy of 0.5 cal./mole can, for example, account for the variation in growth rates observed, 20 deg. from the transition point ($\Delta T = 20^{\circ}$), while a change of 35 cal./mole is required to account for the same variation in growth rates 90 deg. from the transition point ($\Delta T = 90^{\circ}$). Therefore less scatter in growth rates would be expected, but none occurs for pure crystals,

though higher rates are obtained for impure ones. It must be assumed that the retardation is less effective for impure crystals than for pure ones, since the theoretical growth rates should be much higher near the transition point. The theoretical growth rates, without the strain energy correction, and the experimental rates are shown as a function of temperature in Fig. 12.

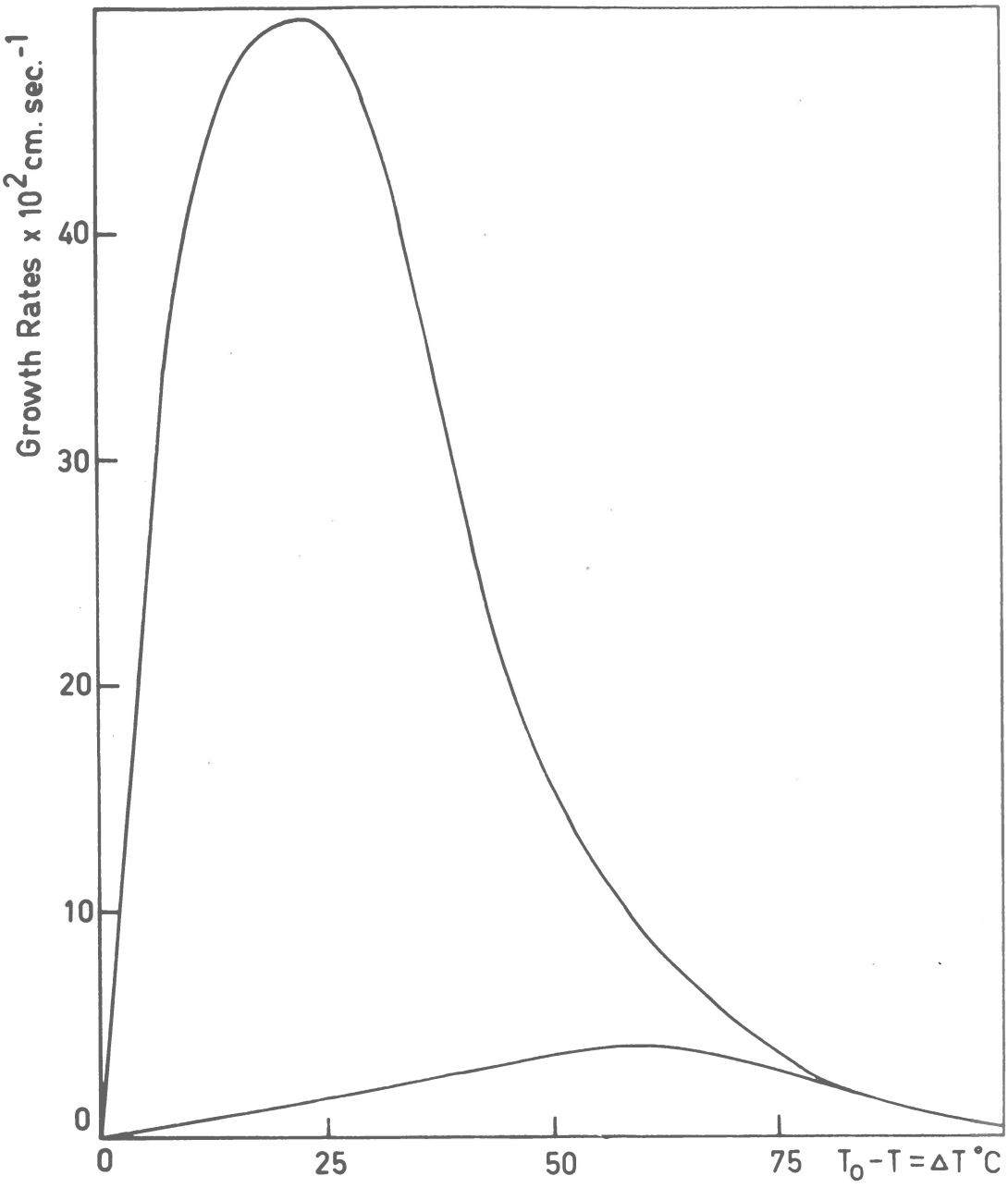

FIG.12 Theoretical and experimental growth rates plotted against temperature on supercooling.

CONCLUSIONS

A brief review of the experimental results will now be given, followed by a short discussion on the possible mechanism, and the implications involved.

The room temperature phase $AgNO_3$ superheated up to 16 deg. (rates measured for $\Delta T = 11^{\circ}$), nucleating spontaneously, and transforming to one or more crystallites, from one or more nuclei. The isothermal growth rates were constant with time, except in the initial stages, when a nucleus appeared in the centre of the crystal, making rates slower. The interface was sharp and straight, and growth rates were dependent on the orientation of the parent phase, the 'b' direction displaying higher growth rates than the 'a' direction by about one third. The growth rates increased exponentially with temperature, reaching 0.52 mm./sec. at 11 deg. superheating. They were consistent for crystals of one size, orientation, purity, and decomposition, but yielded rates which were higher up to a 100% or more with bigger and slightly decomposed crystals. Some of the transforming crystals showed striations, which retarded the transition, and resulted in spasmodic growth rates. $AgNO_3$ whiskers studied showed variable isothermal growth rates.

The high temperature phase could be supercooled to any temperature desired (lowest temperature used was $-30^{\circ}C$), the subsequent transition was initiated by artificial nucleation. As the temperature was lowered

from the transition point, the rates decreased almost linearly (except for the first few degrees), reaching a maximum of 0.394 mm./sec. at ΔT = 58.5 deg., then decreased and went to zero rates at -30°C. The isothermal growth rates were constant with time, forming one or more crystallites, with no apparent correlation between the orientations of the nucleating and transforming crystals. At temperatures below about 30°C. the transition resulted in a mass of crystallites. As on superheating bigger crystals, as well as slightly decomposed ones, gave higher growth rates; whiskers again gave irregular isothermal growth rates. The bending of whiskers was also observed during transformation, as well as striations with ordinary crystals.

When existing growth rate equations were applied to the transition on superheating, a changing activation energy, decreasing with increasing temperature (176 $\longrightarrow$ 86 kcal./mole), was obtained, as well as a high value for the pre-exponential factor; both figures being too high to have any physical significance.

On supercooling an activation energy of 21.1 kcal./mole was obtained, at low temperatures, and a slightly negative value near the transition point. The rates were of the right order, far removed from the transition temperature, and too slow near the transition point.

The transitions were characterised by the presence of stresses, resulting in strains and strain energies. The realness of the strain

energy was confirmed by X-ray photographs, which showed considerable asterism in crystals after a transformation (Fig. 1), as well as cracking, and striations during a transition (Fig. 2). Whiskers were also seen to bent during transformation, and the initial growth rate inside the parent phase was also slower until the edge of the crystal was reached. Growth along the edge was also a little faster than growth through the middle.

When a strain energy was included in Turnbull's growth equation, a single valued activation energy was obtained (147 kcal./mole) for superheating. The maximum strain energy applied (11.4 cal./mole) was not judged to be excessive, as Wolfson, Fine, and Ewald[39] gave a strain energy of 40 cal./mole for the tin transition. The pressure required for slip to occur in $AgNO_3$ was roughly 5×10^4 gm./cm^2.

On supercooling a strain energy correction (maximum value 76.5 cal./mole) resulted in a constant activation energy of 21.1 kcal./mole, throughout the whole temperature range, as well as agreement between theoretical and experimental rates. The strain energy correction was important in the region near the transition point, when the chemical free energy (the driving force of the reaction) was not much bigger than the strain energy which opposes it, while at low temperatures $\Delta G_v \gg \Delta G_s$ so that the strain energy had little significance far away from the transition point.

It is very difficult to elucidate a mechanism for the $AgNO_3$ transitions, and not quite unambiguous, since, for example, on

supercooling, where the activation energy is 21.1 kcal./mole, the vapour intermediate state could apply (Hartshorne's and Bradley's type of transition), as the activation energy is of the right order, The rates are, however, a little too fast for this transition, and the transmission of stresses observed is not quite compatible with an intermediate vapour phase.

Mott's 'island model' equation, which postulates 'n' molecules melting and moving across to the stable phase, agrees with the activation energy observed, when 'n' is assumed to be more than one; but it predicts faster growth rates, by a factor of about 400, than found experimentally, so that it does not seem to apply to the $AgNO_3$ transition.

Turnbull's equation can be applied with more confidence, since it predicts the right experimental rates and, as it does not postulate an intermediate vapour phase, the transmission of stresses across the interface may be possible, the activation energy could correspond to the activation energy for grain boundary diffusion. The mechanism may then be assumed to be an activated process, where the molecules diffuse across a region of poor fit, to form a stable phase; the rate of growth is modified by the stresses set up, owing to the different specific volumes of the two phases (about 1%), and varying crystallographic fit. The resulting deformation produces a variable strain energy, which opposes ΔG_v (the driving force), and results in

variable growth rates along different crystallographic directions, as well as in scatter of growth rates from crystal to crystal. Whiskers, for example, which are fragile, being easily bend on handling, can be strained much more readily and hence irregular and poorly reproducible growth rates are obtained. But large crystals give faster rates than small ones, as do slightly decomposed crystals, and as these may be expected to contain more defects, they should possess a greater strain energy, and thus slower rates, and not bigger ones as observed. The defects, e.g. vacancies, however, may make the interface less coherent and thus less able to transmit stresses, in which case higher growth rates would be expected. Whiskers then, which may be assumed to have a more perfect crystalline structure should have a more coherent interface, which will result in greater transmission of stresses, and therefore in slower and irregular growth rates.

A precise answer to these questions, as well as the exact mechanism involved, can only come from a better knowledge about the nature of the interface and the exact amount of strain involved in the phase transition. Until these questions are answered, the irregular growth rates, and the varying rates with crystal size and orientation, as well as the exact mechanism involved, cannot be explained in an unambiguous way.

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