H. T. Hall

Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 29, No. 7, 1110–1121, July, 1958

On the Quality of Gray Tin Crystals and Their Rate of Growth*†

J. H. BECKER
National Bureau of Standards, Washington, D. C.
(Received June 1, 1956)

Various methods of preparing samples of gray tin suitable for electrical and optical investigations are described. Attempts to deposit atoms of tin directly into the gray tin lattice by vapor- and electrodeposition and by chemical reactions at low temperatures have all yielded crystals of white tin; however, by transformation of white tin under suitable conditions it is possible to obtain large coherent crystals of gray tin. These include samples several cm long showing single crystal regions up to 2 mm, as well as flat thin films as large as 25×25 mm^2.

The temperature at which the transformation takes place, the purity of the initial white tin specimen, its size, and the method of attaching a sample to a substrate are important factors for determining both the quality and the rate of transformation. Investigations were carried out over a wide range of temperatures for several sources of high purity tin, as well as with additions of In, Ga, Al, As, and Sb. Effects of mechanical and thermal treatment are also included. A careful distinction is made between the time for nucleation and the rate of growth after nucleation.

Results are analyzed in the light of absolute rate theory and a reasonable explanation is obtained for many of the observed phenomena. The heat of activation for the white to gray tin reaction is determined as $(8.7\pm1.5)\times10^3$ cal/mole at 0°K.

I. INTRODUCTION

IN recent years interest has developed in the electrical and optical properties of gray tin. The work on the electrical properties by Busch and his co-workers,[1] Kendall,[2] and Blum and Goriunova[3] established that gray tin is a semiconductor with a small forbidden energy gap (~0.1 ev). Extensive studies on crystals of the elements silicon and germanium have resulted in important contributions to our understanding of semiconductors and their practical applications. Gray tin is the last in the homologous series of the semiconducting elements, diamond, silicon, germanium, and gray tin, and their energy band structures are of considerable theoretical interest. Moreover, the small forbidden energy gap of gray tin suggests the possible use of this material as an infrared photodetector.

Fundamental to an accurate determination of the energy band structure of a material are measurements on single crystals. The measurements of gray tin

---

* Research supported by the Office of Naval Research.

† This work is based on a section of a thesis for Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1957 (hereafter referred to as JHB thesis).

[1] Busch, Wieland, and Zoller, Helv. Phys. Acta **23**, 528 (1950); **24**, 49 (1951). G. Busch and E. Mooser, Helv. Phys. Acta **26**, 611 (1953); G. Busch and J. Wieland, Helv. Phys. Acta **26**, 697 (1953).

[2] J. T. Kendall, Proc. Phys. Soc. (London) **B63**, 821 (1950); J. T. Kendall, Phil. Mag. **45**, 141 (1954).

[3] A. I. Blum and N. A. Goriunova, Doklady Akad. Nauk. S.S.S.R. **75**, 367 (1950).

referred to above were made on highly polycrystalline powders and chunks. Recently Ewald,[4] Groen and Burgers,[5] and the author[6] have reported some success in growing crystals of gray tin (which in some cases exhibit single crystal patterns under x-ray analysis[‡]), and electrical measurements have been made on some of these samples.[4,6]

In all cases the samples were produced by direct transformation of white tin. (Extensive attempts by several investigators[7] to prepare gray tin by depositing tin atoms directly into the gray tin lattice were unsuccessful.) It is thus of value to describe in detail some of the factors which influence the quality[§] of gray tin crystals.

The $\beta\leftrightarrows\alpha$ transformation of tin has interested scientists for more than a hundred years. It represents one of the few cases where a common element changes from one solid phase to another. Because of the simplicity of the systems, the transformation is of considerable theoretical interest. Moreover, for pure tin, the rates of transformation are easily measurable over a wide and convenient range of temperatures. The possible destruction of tin objects stored at low temperatures lends additional value to a study of the factors influencing the likelihood for the transformation to begin and the subsequent rate of growth.

In 1851 Erdmann[8] reported on the failure of tin organ pipes as a result of the $\beta\rightarrow\alpha$ transformation. Since then a considerable amount of work has been done by many investigators on the thermodynamic properties of the white-gray tin system and the factors influencing the rate of transformation.

The heat capacity measurements of Bronsted[9] and Lange[10] and the results on the heat of transformation (−532 cal/mole at 0°C[9]) enabled determination of the thermodynamic functions. From these data Bronsted calculated a transition temperature T_0 of 20°C, while Lange finds 22°C. The pressure dependence of T_0 was estimated as -2×10^{-2} °C/atmos. (Recently heat capacity measurements on gray tin have been extended to helium temperatures by Hill and Parkinson,[11] but no transition temperature has been evaluated from these experiments.)

Direct measurements of the transition temperature by Cohen[12] using a gray tin-white tin equilibrium cell gave a value of 20°C for the temperature of transition, while the most recent determination by Cohen and Van Lieshout[13] gives a value of 13.2±0.1°C (from rate data).

It has been found that the transformation from the metallic white tin (β) phase (tetragonal lattice, $a=5.831$ A, $c=3.182$ A at 26°C)[14] to the semiconducting gray tin (α) phase (diamond cubic lattice, $a=6.489$ A at 25°C)[15] is accompanied by a volume increase of about 27%. This explains why generally highly polycrystalline and badly cracked samples result from the transformation.[‖]

The factors affecting the rate of transformation have been studied by determining the "time for the appearance of gray tin spots" (t_a) and the linear or volume rate of growth.[¶] It has been found that large reductions in t_a can result from inoculation of the white tin with gray tin seed crystals or some materials isomorphous with gray tin (InSb and CdTe,[16] or Ge)[17]. A large reduction of t_a also occurred when the white tin was subjected to cold work,[18–20] reactor irradiation,[21] and certain solutions[12,17,22]; previous transformations of white tin[18,19] also decreased the time t_a. On the other hand, t_a was appreciably increased by oxidation of the surface,[18,19] annealing,[18,19] and slow growth of the initial white tin crystal.[23] The magnitude of these effects depends on the temperature of transformation as well

---

[4] A. W. Ewald, Phys. Rev. **91**, 244 (1953); **94**, 1428 (1954); J. Appl. Phys. **25**, 1436 (1954); A. W. Ewald and E. E. Kohnke, Phys. Rev. **97**, 607 (1955); A. N. Goland and A. W. Ewald, Bull. Am. Phys. Soc. Ser. II, **1**, 226 (1956).

[5] L. J. Groen and W. G. Burgers, Koninkl. Ned. Akad. Wetenschap. Proc. **B57**, 79 (1954); L. J. Groen, Nature **174**, 836 (1954).

[6] J. H. Becker, Phys. Rev. **98**, 1192 (1955).

[‡] The only reference found in the early literature regarding the production of massive, but badly cracked, gray tin samples is a note in one of the papers by Cohen and Van Lieshout, Z. physik. Chem. **A178**, 221 (1936).

[7] L. J. Groen, Koninkl. Ned. Akad. Wetenschap. Proc. **B57**, 122 (1954). Personal communications: J. T. Kendall and G. Busch.

[§] The quality is defined in terms of the number of cracks per cm^2 of surface and the grain size of the gray tin crystals.

[8] O. L. Erdmann, J. Prakt. Chem. **52**, 428 (1851).

[9] J. N. Bronsted, Z. physik. Chem. **88**, 479 (1914).

[10] Fritz Lange, Z. physik. Chem. **110**, 343 (1924).

[11] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

[12] Ernst Cohen, Z. physik. Chem. **A30**, 601 (1899).

[13] E. Cohen and A. K. W. A. Van Lieshout, Z. physik. Chem. **A173**, 32 (1935).

[14] H. E. Swanosn and E. Tatge, Natl. Bur. Standards (U. S.) Circ. 539, **I**, 25 (1953). (Also contains earlier references.)

[15] See reference 14, **II**, 12 (1953).

[‖] Extensive x-ray investigations by E. O. Hall (Symposium on the *Mechanisms of Phase Transformations in Metals*, Institute of Metals, London, 1955) and K. Kuo and W. G. Burgers [Koninkl. Ned. Akad. Wetenschap. Proc. **B59**, 288 (1956)] revealed no orientation relationships between the white and gray tin crystals. Distortion of the white tin lattice in the neighborhood of the transformation front was observed.

[¶] Survey articles: C. E. Homer and H. C. Watkins, Metal Ind. (London), p. 364 (1942). R. R. Rogers and W. R. G. Stewart, Investigation No. MD2609, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, November 23, 1949. L. J. Groen's thesis (Leiden, October, 1956) contains a more recent survey (in Dutch), as well as the results of his extensive investigation of both the white to gray and gray to white tin transformations, by linear and volume rate of growth techniques (hereafter referred to as LJG thesis).

[16] N. A. Goriunova, Doklady Akad. Nauk S.S.S.R. **75**, 51 (1950).

[17] R. R. Rogers and J. F. Fydell, J. Electrochem. Soc. **100**, 161 (1953).

[18] Cohen, Cohen DeMeester, and Van Lieshout, Z. physik. Chem. **A173**, 169 (1935). E. Cohen and A. K. W. A. Van Lieshout, Z. physik. Chem. **A177**, 331 (1936); **A178**, 221 (1936).

[19] G. Tammann and K. L. Dreyer, Z. anorg. u. allgem. chem. **199**, 197 (1931).

[20] H. Ishikawa, J. Phys. Soc. Japan **6**, 531 (1951). E. S. Hedges, Nature **169**, 621 (1952).

[21] J. Fleeman and G. J. Dienes, J. Appl. Phys. **26**, 652 (1955).

[22] L. J. Groen, reference 7.

[23] C. W. Mason and W. D. Forgeng, Metals and Alloys **6**, 87 (1935).

as the kind and amount of impurities present. Additions of small quantities of Al, Zn, Mg, Te, Co, and Mn to Banka tin (99.95% purity) were found to decrease considerably the time t_a in cold worked and subsequently refrigerated samples.[18] Little or no effect was observed when Fe, Ni, or Cu were added, while t_a increased appreciably for samples containing Bi, Sb, Pb, Au, Cd, and Ag.[18,19,24]

The linear rate of growth (after nucleation) has been investigated over a significant temperature range in "pure tin".[19,25] These measurements indicate that the temperature of maximum rate of transformation lies between −30 and −35°C. (Volume rate of growth measurements gave a maximum at about −50°C.[12,26]) The effect of specific impurities on the linear rate of growth has been studied by Tammann and Dreyer[19] (Pb, Sb, Cd, and Bi) and by Rogers and Fydell[17,24] (for about 10 types of impurities). Most of the work of the latter authors, however, dealt with thin films on a metal substrate for which the growth rate is a sensitive function of the film thickness and bonding to the substrate. Groen's thesis work clearly indicated that the temperature of maximum rate of transformation is increased (to about −20°C) by additions of 0.1% by weight of Hg.

Komar and Ivanov[27] have also measured the rate of transformation as a function of temperature and pressure. It appears that the growth rate can be vastly decreased by high pressures (90 atmos).

Of considerable importance to the use of gray tin is the discovery by Ewald[4] that samples of gray tin containing 0.75 weight percent germanium did not reconvert to white tin when exposed to room temperature for many months, whereas the pure material retransformed within a few hours under the same conditions.

Several authors have applied rate theories to the $\alpha \rightleftarrows \beta$ Sn reaction. Stephenoff[28] reported excellent agreement between theory and experiment for both tin transformations. Unfortunately neither details of the theory nor experimental data were presented. Dunkerly and Mudge[29] analyzed their dilatometer studies in terms of various types of reactions (first order, autocatalytic, etc.). They concluded that both tin reactions were described best by a first-order process (rate of concentration change proportional to concentration) with activation energies 180 cal/mole ($\beta \rightarrow \alpha$) and 2300 cal/mole ($\alpha \rightarrow \beta$).

By considering Avrami-type rate equations,** Groen concluded (LJG thesis) that his data on the white to gray tin transformation were consistent with a constant nucleation rate as well as a constant isotropic linear rate of growth after nucleation; however, no activation energy for the processes could be determined. On the other hand, for the $\alpha \rightarrow \beta$ transformation activation energies of 50 kcal/mole and 120 kcal/mole were evaluated for nucleation and linear growth, respectively. There was some evidence that the nucleation processes did not proceed at a constant rate.

Absolute rate theory was applied by Cagle and Eyring[30] to the data of Tamman and Dreyer[19] on the linear rate of transformation of white to gray tin. They reported good agreement between experiment and theory in which the transformation process was considered to take place by "gray-white tin atom complexes." It was concluded that only a small fraction (10^{-10} to 10^{-13}) of the interface atoms were at reactive sites and the heat of activation was 2600 cal/mole (see Sec. III for further discussion and comparison with the present work).[31]

The purpose of the present investigation was to obtain crystals of gray tin which would be suitable for electrical or optical measurements and to study the kinetics of the $\beta \rightarrow \alpha$ Sn transformation. A detailed study was made of the factors influencing the quality of gray tin crystals. It appears that the crystal quality is influenced by sample size, temperature of transformation, and impurity content, as well as the method of attaching the white tin samples to the substrate. It is shown that gray tin can be prepared as thin films or as bulk samples. The largest single crystals produced were about 2 mm long.

In the investigation of the kinetics of the transformation we have concentrated chiefly on a determination of the linear growth rate after nucleation for high purity tin and tin containing several impurities.

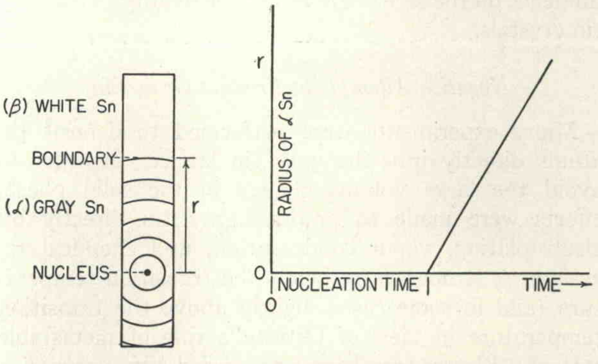

FIG. 1. Growth of gray tin from one nucleus. Sample refrigerated at Time=0.

---

[24] R. R. Rogers and J. F. Fydell, J. Electrochem. Soc. **100**, 383 (1953).

[25] A. Komar and B. Lazarev, Physik. Z. Sowjetunion **7**, 468 (1935).

[26] Ernst Cohen, Z. physik. Chem. **A35**, 588 (1900).

[27] A. Komar and K. Ivanov, Zhur. Eksptl. i Teoret. Fiz. **6**, 256 (1936).

[28] N. I. Stephenoff, Ann. inst. physik. Chem. (Leningrad) **2**, 500 (1924).

[29] F. J. Dunkerly and W. L. Mudge, Jr., Technical Report, University of Pennsylvania, Contract NObs-2477, Navy Department, Bureau of Ships (January, 1950).

** See Sec. III for survey articles by Turnbull; also M. Avrami, J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940).

[30] F. Wm. Cagle, Jr., and H. Eyring, J. Phys. Chem. **57**, 942 (1953).

[31] J. H. Becker, Bull. Am. Phys. Soc. Ser. II, **2**, 45 (1956).

We have studied the transformation process over a wide range of temperatures by measuring the change in the position of the $\alpha-\beta$ boundary. With this method it is possible to determine a nucleation time for the individual spots and the rate of growth after nucleation. Figure 1 illustrates this point. Variations of the rate of transformation with impurity content and sample size, as well as with mechanical and thermal treatment, were determined. It appeared that the time of nulceation also depends on these factors.

II. EXPERIMENTAL

a. Sample Preparation

Source

The pure tin used in these experiments was purchased from the Vulcan Detining Company [manufacturer's designation: V5985 (Lot No. 1) and VS25SP (Lot No. 2)], and from Johnson-Matthey and Company, Ltd. [manufacturer's designation: JMS No. 2356 (Lot No. 3)]. The manufacturers' analyses of these materials in weight percent are:

Lot No. 1—99.995% Sn, 0.003% Fe, 0.0008% Sb, 0.0004% Cu, trace of Pb and Bi(?).

Lot No. 2—99.999+% Sn, no detectable metallic impurities, possibility of traces of Sb less than 0.0005% and Pb, Fe, Cu, Ni less than 0.00001%.

Lot No. 3—Spectroscopically pure tin: 99.9963% Sn, 0.002% Pb, 0.001% Sb, 0.0045% Fe, 0.001% Cu, 0.00007% S, 0.00004% Bi, 0.00002% As.

A spectrochemical analysis of each of these materials, before and after the addition of impurities, was obtained (see JHB thesis). For most of the impurities, the amounts measured are in qualitative agreement with the manufacturer's analysis. The method of growing thin films (see below) consistently introduced small amounts of Cu, Fe, and Ni which showed, however, no influence on the rate of growth or the quality of the gray tin crystals.

Negative Attempts to Produce Gray Tin

Many experiments were performed to deposit tin atoms directly into the gray tin lattice. In order to avoid the large volume change in the solid phase, efforts were made to produce gray tin directly by electroplating, vapor condensation, and chemical reactions at temperatures below the transition temperature (and in some cases slightly above the transition temperature in view of Ostwald's rule of metastable states[32]). Electrodeposition was carried out over a wide range of temperatures (between 50°C and −78°C) with rates of deposition varying from 100 A per week to 1 mm per hour. Various electrolytic solutions were used involving tin as positive ions, and as negative ion radicals and complexes. The substrates included gray tin seed crystals, InSb, Ge, Cu, Pt, and Nichrome.

Vapor deposition was carried out in a bell-jar evaporator with a vacuum of 10^{-5} mm Hg. The substrate temperature ranged from 25°C to −30°C, with similar substrates and rates of deposition as in the electroplating experiments. Additional substrates of infrared transparent crystals (NaCl, KCl, KBr, KI, and CsBr) were also tried.

The chemical experiments performed near 0°C were replacement of tin ions by zinc and reduction of an aqueous solution of tin by Ti^{3+} ions with seed crystals of gray tin present.

Positive Attempts: Transformation of White Tin Crystals

Several kinds of white tin samples were used in these experiments. Large single crystals of white tin were cut from the various commercially available lots of white tin and milled to the specified size. Thin single crystals (0.025 to 0.2 mm) were easily grown by "sandwiching" the appropriate thickness white tin sheets between glass plates, clamping the system in a high-purity carbon mold and allowing recrystallization from one end during a single pass in a zone refiner. Polycrystalline samples were produced by pressing and subsequent rolling at room temperature to thicknesses as small as 0.01 mm. The samples were cleaned in CCl_4, acetone, and distilled water, and sometimes etched with dilute HCl.

Additions of small amounts of metallic impurities (Al or Sb) were achieved by melting the high purity tin together with the appropriate quantities of these metals and pulling a single crystal using the Kyropoulos technique.[33] One crystal was doped with Al and zone refined to produce a continuous gradation of impurity content (see JHB thesis). Larger additions of Al, Sb, Ga, etc. were accomplished by melting the tin with these metals in a sealed and evacuated Pyrex tube. The recrystallization rate for the single crystal growth and zone refining was about 2 in. per hr; for the sealed-tube method of crystal growth, cooling from 400°C to room temperature took place in about 6 hours.

Thin films were produced by rapid evaporation in vacuum onto a substrate at room temperature or by electroplating.[††]

In order to study the effect of bonding, samples were attached to a copper substrate with various cements. The cements used were those which would give a range of bonding from very hard and strong to very pliable and weak and included soft solder, Duco cement, Unicorn stop-off, and GE cement No. 7031.

For the investigation of the effects of mechanical and thermal treatment, the white tin samples were sub-

---

[32] W. Ostwald, Z. physik. Chem. 22, 306 (1897).

[33] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. 96, 571 (1954).

[††] Sodium Stannate Bath: W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming* (McGraw-Hill Book Company, Inc., New York, 1949), p. 330.

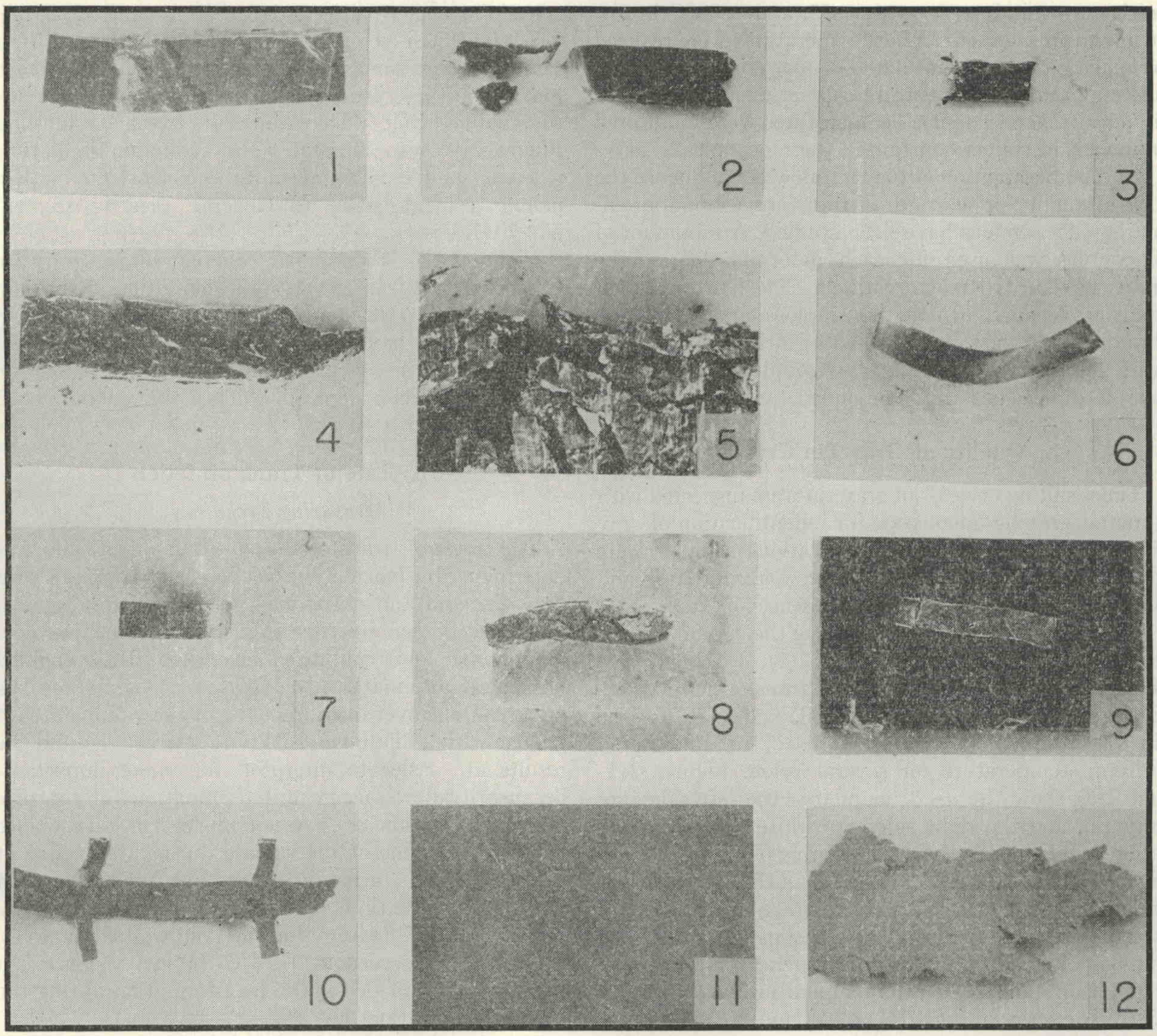

FIG. 2. Photographs of gray tin samples. (The specimens are completely gray tin except for those shown in photographs 1 and 3 where the right sides are white tin.) Magnification 4.3 ×.

Photograph No.	Sample[a]	Temperature of transformation °C	Thickness mm
1	Lot No. 1 tin	5	0.025
2	Lot No. 1 tin	−30	0.025
3	Lot No. 1 tin	−78, 5[b]	0.025
4	Lot No. 1 tin	5	0.25
5	Lot No. 1 tin	5	4.0
6	Lot No. 1 +1% Ga	− 6	0.11
7	Lot No. 1 +1% As	− 6	0.11
8	Lot No. 1 +0.0025% Sb	+ 5	0.50
9	Lot No. 1 +0.0025 Al	− 6	0.11
10	Lot No. 2 +0.025% Al Zone refined 14 cm	− 6	0.11
11	Electroplate	−30	0.0005
12	Electroplate[c]	−30	0.020

[a] The added amount of impurity is listed in atomic %.
[b] Growth was initially at −78°C, and continued during storage at 5°C.
[c] The sample broke loose from the substrate during the transformation.

jected to various treatments ranging from hot and cold work to annealing. Hot work consisted of pressing and rolling at room temperature, while cold work was achieved by pressing at −195°C. The annealing treatment varied from holding the sample at room temperature for several years to exposing the specimen to 110°C for several hours.

The white to gray tin transformation was started by pressing a seed of gray tin on one end of the sample. For the determination of the nucleation time the samples were not seeded.

The different low temperatures used for the study of the transformation were achieved as follows: Temperatures of 5, 0, and −6°C were obtained in a commercial refrigerator, and −30, −41, −55, and −60°C in low temperature cabinets. Other temperatures were realized by placing thermally insulated copper boxes containing heaters in a low temperature cabinet or in dry ice and liquid nitrogen systems. Temperatures were monitored by means of copper-constantan thermocouples.

In the investigation of the factors which influence the crystal quality or the rates of transformation, approximately 400 samples have been studied. A minimum of 5 samples was used for each determination of the influence of a particular variable. The linear rates of transformation shown in the graphs and figures were determined from samples whose width and thickness were sufficiently small that L was independent of the sample dimensions (for nonbonded samples).

b. Quality of Gray Tin Crystals

The resulting crystals of gray tin were inspected with a metallographic microscope for indentification of gray tin and quality determination. Various samples were examined with x-rays for grain size determination and positive identification of the presence of gray tin.‡‡

The results of the factors affecting the crystal quality are illustrated in Fig. 2. Figures 2(1), 2(2), and 2(3) show a series of white tin crystals transformed, respectively, at temperatures of 5, −30, and −78°C. The tin was from lot No. 1, rolled to 0.025 mm and stored at room temperature for several years. Figures 2(1) and 2(3) show the $\alpha-\beta$ boundary; the left sides are gray tin, and the right sides are white tin. All of the other samples of Fig. 2 consist entirely of gray tin. For a given thickness, purity, and mechanical treatment, it will be seen that as the *temperature of transformation* is decreased, the quality of the crystals decreases. The number of cracks per unit area generally increases by a factor of about 2–3 as the temperature is lowered by 15°C. The series of Figs. 2(1), 2(4), and 2(5) illustrates the decrease of crystal quality with increase of *sample size* for the same purity of tin and temperature of transformation (lot No. 1, transformed at 5°C). The thickness of these samples is, respectively, 0.025 mm, 0.25 mm and 4 mm. Another difference between these samples is that the specimen of Fig. 2(4) had been subjected to some "hot work" (rolling at room temperature shortly before refrigeration) while Figs. 2(1) and 2(5) show annealed specimens. From this and several other experiments one can conclude that *mechanical working* of the white tin results in poorer quality gray tin crystals.

Figures 2(6), 2(7), 2(8), and 2(9) illustrate the results of additions of, respectively, 1% Ga, 1% As, 0.0025% Sb, and 0.0025% Al (atomic percent) to lot No. 1 tin. The sample of photograph 10 consists of lot No. 2 tin containing essentially 0.01–0.1% Al and Cu, and 0.001–0.01% Si (see JHB thesis). A comparison of these samples gives some idea about the influence of *impurities* on the crystal quality: Ga, As, and Al increase the quality, while a decrease results from Sb additions. Figure 2(9) also illustrates the reduction in curling when a sample is attached to the substrate with a pliable cement such as General Electric Cement No. 7031.

Figure 2(11) shows a flat coherent film of gray tin which resulted from a very thin deposition of tin on a nichrome substrate.

Finally, we have presented in Fig. 2(12) a (free) piece of gray tin which broke loose from the substrate. This occurs when deposits thicker than about 0.005 mm are used.

c. Rate of Transformation

Measuring Technique

The rate of transformation after nucleation was determined by inoculating one end of a sample with a gray tin seed and observing the position of the $\alpha-\beta$ boundary at definite time intervals with a low-power microscope and calibrated eyepiece. This enabled position determinations to 1/60 mm. This method has an advantage over measurements of the volume rate of change with a dilatometer because it is simpler and the results are easier to interpret, but more important, because it allows accurate determinations of the rate of transformation even when nucleation takes place at several regions of the sample during the course of the experiment. During the measurement of the position of the gray-white tin boundary the samples were usually brought to 0°C (except for the cold-worked samples, which were observed at −78°C). When necessary, a correction was made for the transformation during the time of observation.

The time for self-nucleation (t_n) was determined by observing the position of the gray tin spot when it was a finite size and the linear rate of growth of the spot was used to determine when its size had been zero [see Fig. 1].§§ Samples were handled with noncontaminated instruments and placed in containers to reduce accidental seeding with crystallites of gray tin; nevertheless, the values of t_n represent only a lower limit to the self nucleation time because of the possible influence of "the laboratory being contaminated with gray tin." ‖ ‖

Results can be summarized as follows:

1. The transformation starts on or near the surface of a crystal and growth proceeds radially in all directions with uniform velocity except in the case of large crystals,

---

‡‡ The author wishes to thank Barbara Sullivan and H. Swanson of the Microstructure Section of the National Bureau of Standards for the identification measurements, and N. Koenig and C. Newton of the Metallurgy Division for the grain size determinations.

§§ This method has also been used by Rogers and Fydell.[17, 24]

‖ ‖ Before receiving a shipment of gray tin crystals we were unable to cause a transformation of our white tin, even after mechanical working of the tin or contact with electrolytic solutions. Since then, under identical conditions, spontaneous transformation has taken place.

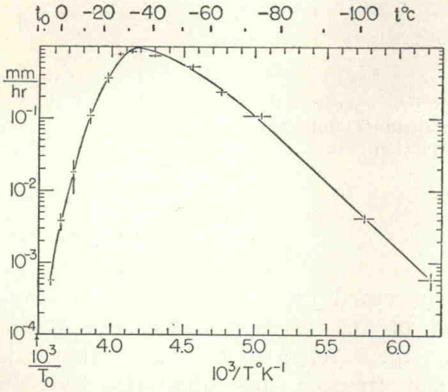

FIG. 3. Linear rate of transformation after nucleation *vs* temperature for high purity tin (Lot No. 1). Each point represents the average of ten to twenty determinations. The rms deviations are also shown. Sample size: 20×1.5×0.025 mm.

where the growth rate near the surface is larger than that in the interior of the crystal.

2. The time for the formation of nuclei of gray tin is considerably decreased by seeding with gray tin and cold working; it is appreciably increased by annealing, by surface oxidation, by raising the temperature, and by decreasing the sample size. Six samples from lot No. 1, which were annealed at room temperature, (dimensions 20×2×0.5 mm) showed no nucleation within the time of observation (6 months at −30°C, 1 month at −78°C). Slight working at room temperature (10% reduction in thickness) gave nucleation in 10 to 30 hours. Cold work at −195°C (decreasing the thickness from 25 to 0.5 mm) reduced t_n further to 2–4 hours. Vacuum annealing for 6 hours at 110°C raised the nucleation time to about 100 hours. In all these cases the transformation was observed at −30°C and at −78°C, with very little difference of nucleation time at these two temperatures. The rate of growth after nucleation was, however, independent of mechanical treatment and surface conditions. The behavior of lot No. 2 tin was similar; however, for lot No. 3 tin t_n decreased more rapidly when the thickness was increased or when the samples were subjected to mechanical work.

3. The linear growth rate (after nucleation) increased rapidly when the temperature was lowered below 5°C. It reached a maximum in the range −20 to −35°C and then decreased more slowly towards lower temperatures. Figure 3 shows the linear rate of transformation as a function of temperature for one source of high purity tin (lot No. 1). The maximum rate of transformation (1.0 mm/hr) occurred at −30°C, while at 7°C and −107°C the rate was 10^{-3} times smaller.

4. Impurities in the white tin (both the kind and the amount of the addition are important) change the magnitude of the transformation rate considerably. Figure 4 illustrates this point; curves are shown for each of the three sources of high purity tin and for a few samples of tin with added impurities (Al, Ga, As). Also included for comparison are the data of Tammann and Dreyer[19] on pure Kahlbaum tin (believed to be about 99.95% pure). Table I indicates the value of the growth rate at −30°C for a wide variety of impurity contents. It is interesting to note that small amounts of Al in lot No. 1 tin increased the rate, while larger amounts reduced the growth rate again.

5. The rate of transformation in rather thin samples is considerably decreased when the specimen is cemented to a substrate. In thicker samples the influence of bonding is small.

6. The size of free samples (for thicknesses ranging from 0.01 to 1 mm) does not seem to affect the rate of growth. However, in very thin films (on a substrate), the thickness influences the transformation rate enormously. Rates of 10^{-3} to 10^{-4} mm/hr have been measured in films of the order of 1 micron, while layers of 0.1 mm show growth rates which are 100 to 1000 times higher.

III. RATE THEORY

Various approaches have been used to calculate the rates of physical and chemical reactions.[34–39][¶¶] For a

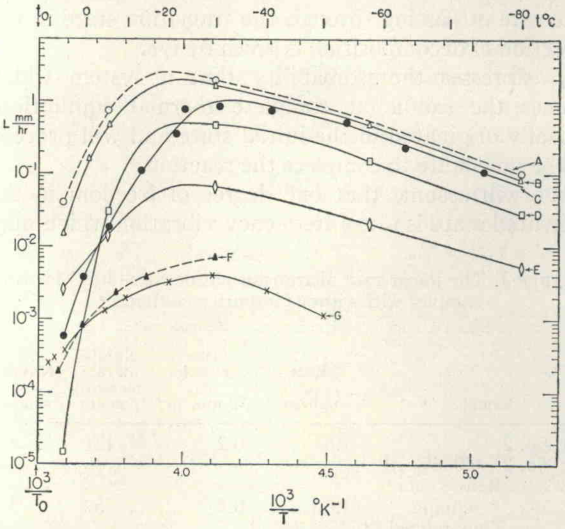

FIG. 4. Linear rate of transformation after nucleation *vs* temperature for tin samples of different impurity content. Sample size: 20×1.5×0.1 mm. (A) Lot No. 1+0.002% (atomic) Al; (B) lot No. 2 (high purity tin); (C) lot No. 1 (high purity tin); (D) lot No. 1+1% (atomic) As; (E) lot No. 1+1% (atomic) Ga; (F) lot No. 3 (high purity tin); (G) Kahlbaum tin (data of Tammann and Dreyer).

---

[34] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[35] H. Eyring, J. Chem. Phys. **3**, 107 (1935).

[36] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

[37] C. A. Wert, Phys. Rev. **79**, 601 (1950). C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949). C. Zener, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952).

[38] J. O. Hirschfelder and E. Wigner, J. Chem. Phys. **7**, 616 (1939).

[39] W. Primak, Phys. Rev. **100**, 1677 (1955).

[¶¶] Excellent discussions by D. Turnbull on phase transformations can be found in *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955) and in *Solid State Physics* (Academic Press, Inc., New York, 1956), Vol. 3.

process involving an activation energy, one assumes that the system passes from the *initial* state to the *final* state primarily along the paths which require the minimum increase in free energy. Such a reaction path for the white-gray tin system is shown schematically in Fig. 5. The energy increases for directions (not shown) away from the reaction path. The saddle point along the route connecting the initial and final states is called the *transition* or *activated* state, which has an assumed width δ. By postulating that equilibrium exists between the initial and final states, the *rate coefficient* K can be presented in the form[34]:

$$K=\gamma(\bar{v}/\delta)(f_t/f_i)\exp(-E_0/kT)$$
$$=\gamma(\bar{v}/\delta)\exp[-(G_t-G_i)]/kT, \quad (1)$$

where γ is the transmission coefficient, $\bar{v}$ represents the average velocity at the transition state in the direction to complete the reaction, f is the partition function, E_0 equals the minimum energy of the transition state minus that of the initial state at 0°K. G's are the Gibbs free energies while i and t refer to the initial and transition regions. In Eq. (1), the exponential factor represents the fraction of the system which is activated. The rate of passing through the transition state in the direction of decomposition is given by $\bar{v}/\delta$.

γ expresses the probability that a system which crosses the saddle at complete thermal equilibrium actually originated in the initial state and will proceed to the final state to complete the reaction.

We will assume that one degree of freedom in the activated state is a low frequency vibration which may be approximated by a translational motion in the direction of the reaction coordinate. With $f_t=f_t^*\times f_{\mathrm{transl}}$ (the * refers to the fact that one degree of vibrational freedom has been removed from the function), it follows[34] that

$$K=\gamma\frac{kT}{h}\frac{f_t^*}{f_i}\exp(-E_0/kT)$$
$$=\gamma\frac{kT}{h}\exp[(G_t^*-G_i)/kT]. \quad (2)$$

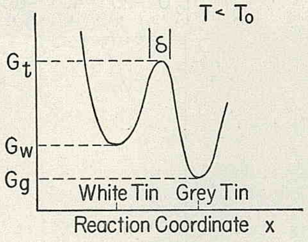

FIG. 5. Free energy of tin atom *vs* distance along the transformation path.

TABLE I. The linear rate of transformation at −30°C for tin samples with various impurity contents.[a]

Sample	Rate L mm/hr	rms deviation ΔL ±mm/hr	Number of rate measurements	Number of samples
Lot No. 2	1.6	0.2	12	4
Lot No. 2+0.025% Al				
Before zone refining	1.6	0.2	5	5
Zone refined				
0 cm	1.7	0.3	11	4
7 cm	1.5	0.1	11	4
14 cm	1.2	0.3	8	4
Lot No. 3	7×10^{-3}	1×10^{-3}	8	4
Lot No. 1	0.90	0.05	20	12
Lot No. 1+0.0025% Al	1.8	0.2	13	4
Lot No. 1+0.1% Al	0.5	0.2	6	4
+0.1% Ga	1.1	0.2	4	4
+0.1% In[b]	1.9×10^{-2}	0.1×10^{-2}	7	2
+0.1% As	0.4	0.1	5	4
+0.1% Sb	0.1	0.05	9	5
Lot No. 1+1% Al	0.1	0.05	9	2
+1% Ga[c]	6.6×10^{-2}	0.9×10^{-2}	11	6
+1% In	No trans. 9 months			
+1% As[d]	0.45	0.05	4	4
+1% Sb	No trans. 9 months			

[a] Added amounts of impurities are given in atomic %. Sample size 20×1.5×0.1 mm.
[b] 3 samples not listed here showed no transformation in 9 months, even though all samples were inoculated with a gray tin seed.
[c] 2 samples not listed here gave a rate 0.8±0.1 mm/hr.
[d] 2 samples not listed here gave a rate 2.0±0.2 mm/hr.

Application to the $\beta\rightleftarrows\alpha$ Tin Transformation

For a description of the growth after nucleation it is assumed that only the atoms adjacent to the white-gray tin boundary take place in the reaction, and only a fraction (A) of these interface atoms are at *reactive* sites. The latter probably are highly stressed regions surrounding a gross imperfection where a smaller activation energy is required for an atom to jump. The postulate that growth takes place only at the boundary is supported by x-ray and visual observations which have indicated no mixing of the α and β phase except perhaps in the interface region.

There is a continuous exchange of reactive atoms of white and grey tin, and below the transition temperature the net growth produces gray tin. The resulting number of cracks and imperfections is a measure of the brittleness of the material and the amount of stress introduced into the lattice by the transformation. These depend upon impurity content and temperature, so the number of reactive sites (=A times the number of interface atoms) will depend upon these factors. Introduction of those impurities which cause the tin to become less malleable, as well as decreasing the temperature of transformation, is expected to increase A.***

The Debye temperatures of bulk white and gray tin are 198°K and 253°K[9] or 260°K,[11] respectively, and the heat of transformation for the $\beta\leftrightarrows\alpha$ reaction is small.[9] It follows from the considerations of Hirschfelder and Wigner[38] that the transmission coefficient is virtually temperature independent and close to unity for approaches to the barrier from either direction.

For single atom jumps Eq. (2) gives the rate coeffi-

*** This leads to $dA/dT<0$. Further discussion of A is included in Sec. IV.

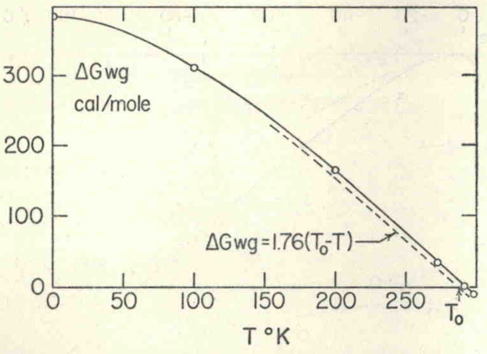

FIG. 6. Gibbs free energy difference of white and gray tin *vs* temperature. The solid curve is from Bronsted's heat capacity and heat of transformation data. The dashed curve represents adjusted values which give $\Delta G_{wg}=0$ at a transition temperature (T_0) of 286.4°K.

cients of the forward (K_1) and reverse (K_{-1}) reaction:

$$K_1=\frac{kT}{h}\exp-(G_t^*-G_w)/kT,$$
$$K_{-1}=\frac{kT}{h}\exp-(G_t^*-G_g)/kT. \tag{3}$$

We will use the notation $G_t^*-G_w\equiv\Delta G^*=\Delta H^*-T\Delta S^*$, $G_t^*-G_g=\Delta G^*+\Delta G_{wg}$, for the free energies, heats, and entropies, where the subscripts w or g refer to white and gray tin.

The linear rate of transformation L is:

$$L=DA(K_1-K_{-1}), \tag{4}$$

where D is the average distance moved by the boundary when a single atom jumps from a white to gray tin site. For polycrystalline material the average value of D is

$$D=\frac{a_g}{N_g^{\frac{1}{3}}}-\frac{(a_w^2c_w)^{\frac{1}{3}}}{N_w^{\frac{1}{3}}}. \tag{5}$$

In Eq. (5), a and c refer to the lattice constants while N is the number of atoms within this cell ($N_g=8$; $N_w=4$). The final expressions for the rate of transformation become:

$$\begin{aligned}L&=\frac{kT}{h}AD\exp(-\Delta G^*/kT)[1-\exp(-\Delta G_{wg}/kT)]\\&=\frac{kT}{h}AD\exp(+\Delta S^*/k)\exp(-\Delta H^*/kT)\\&\qquad\times[1-\exp(-\Delta G_{wg}/kT)].\end{aligned} \tag{6}$$

The heat of activation ΔH^* is related to the slope W of

$$\ln\{L/[(kT/h)D(1-\exp(-\Delta G_{wg}/kT)]\}\ vs\ 1/T.$$

Using the thermodynamic relationship $T(dS/dT)=(dH/dT)$, it follows that

$$W=-\frac{T^2}{A}\frac{dA}{dT}-\frac{\Delta H^*}{k}. \tag{7}$$

With ΔG_{wg} shown in Fig. 6††† and L from Fig. 3, the function $Y\equiv L/\{(kT/h)D[1-\exp(-\Delta G_{wg}/kT)]\}$ has been calculated. It is presented in Fig. 7.

At the lowest temperatures this curve approaches a straight line. Since the temperature dependence of the heat of activation is usually small,[34] the straight line region in Fig. 7 can result only if $(T^2/A)(dA/dT)$ is either negligible compared to $\Delta H^*/k$, or temperature independent. The latter seems fortuitous and it will be assumed that the slope W at low temperatures gives a good approximation for $\Delta H^*/k$. One obtains $\Delta H^*=8.7\pm1.5\times10^3$ cal/mole. (Since we reason $dA/dT<0$, this value is a lower limit for ΔH^*.) For the model which we have used in these derivations, the one degree of translational freedom in the activated state contributes 5/6 RT cal/mole to the heat of activation. Thus $\Delta H=\Delta H^*+5/6RT$ and one obtains $\Delta H=8.7\sim1.5\times10^3$ cal/mole at 0°K and 9.1×10^3 cal/mole at 273°K.‡‡‡

In order to obtain the entropy of activation, and also the temperature dependence of ΔS^* and ΔH^*, it would be necessary to make further assumptions concerning the activated state. Methods for estimating the vibrational frequencies in the transition state have been

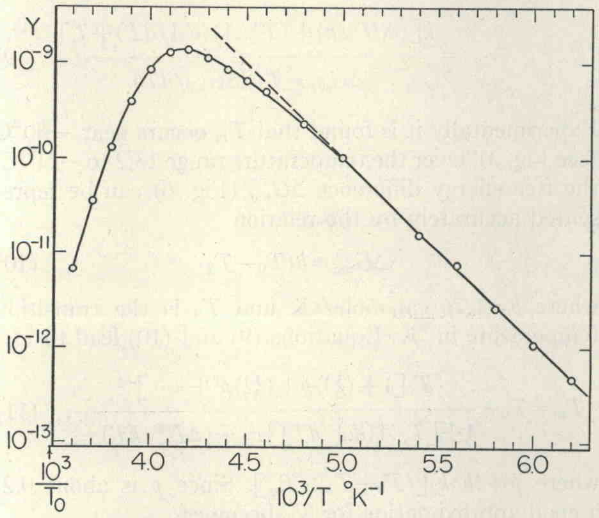

FIG. 7. Plot of the function Y *vs* $10^3/T$. The slope $=-(T^2/A)\times(dA/dT)-(\Delta H^*/k)$. L is from Fig. 3, ΔG_{wg} is from Fig. 6.

---

††† The free energy values ΔG_{wg} used for calculations in this paper are taken from the dashed curve of Fig. 6. This was constructed from the most recent value of the transition temperature, 13.2°C,[13] and the temperature dependence of the free energies for bulk white and gray tin found by Bronsted[9] (solid curve in Fig. 6). Since large stresses exist at the white-gray tin interface, the *bulk* free energy differences give only an approximation for the free energy difference ΔG_{wg} of the *reactive* atoms.

‡‡‡ The temperature variation of ΔH^* is not included in these values (see the following discussion).

suggested.[40] As a refinement these may be worthwhile; however, for an estimate of ΔS^* we use Zener's empirical relation[37] obtained from self diffusion in metals:

$$\Delta S=\beta(\Delta H/M). \tag{8}$$

ΔS and ΔH are the entropies and heats of activation. M is the melting point in °K, while β is a constant for each metal. With the value $\beta=0.50$ (i.e., for lead[37]) and ΔH^* from above, the entropy of activation becomes $\Delta S^*=8.7\pm0.6$ cal/mole/°K.

Figure 8 shows the theoretical rate curves from Eq. (6) calculated with temperature independent ΔH^*, ΔS^*, and A. The solid curve (b) was obtained from the average values of the heat and entropy of activation just presented, while the lower experimental limits of ΔH^* and ΔS^* give the dashed curve (a). The corresponding values of A (1.7×10^{-2} and 7.6×10^{-4}) were determined so that the maximum rate of the theoretical curves would equal that of the experimental data. The calculated curves show the qualitative features of the experimental data; however, T_m is displaced to higher temperatures.

We believe the shift of T_m stems mainly from the fact that a constant value of A was used in calculating the theoretical curve of Fig. 8. This can be shown as follows:

Equating the temperature derivative of L in Eq. (6) to zero at $T=T_m$ one obtains

$$-1+\exp(\Delta G_{wg}/kT)=\frac{k[(\Delta H^*/k)+(T^2/A)(dA/dT)+T]}{\Delta G_{wg}-T(d\Delta G_{wg}/dT)}. \tag{9}$$

Experimentally it is found that T_m occurs near -30°C (see Fig. 3). Over the temperature range 13.2 to -50°C, the free energy difference ΔG_{wg} (Fig. 6) can be represented accurately by the relation

$$\Delta G_{wg}=b(T_0-T) \tag{10}$$

where $b=1.76$/cal/mole/°K and T_0 is the transition temperature in °K. Equations (9) and (10) lead to

$$T_m=T_0-\frac{T_0[1+(\tfrac{1}{2}!)p+(\tfrac{1}{3}!)p^2+\cdots]^{-1}}{1+[T/A(dA/dT)]_{T_m}+(\Delta H^*/kT)_{T_m}}, \tag{11}$$

where $p\equiv(b/k)[(T_0-T_m)/T_m]$. Since p is about 0.2, a good approximation for T_m becomes

$$T_m=T_0-\frac{T_0}{1+[T/A(dA/dT)]_{T_m}+(\Delta H^*/kT)_{T_m}}. \tag{12}$$

The value of T_m is not sensitive to small deviations from Eq. (10). Thus at $T=240$°K (i.e., T_m), one calculates $(1/A)(dA/dT)=-5.5\times10^{-2}$ from Eq. (12).

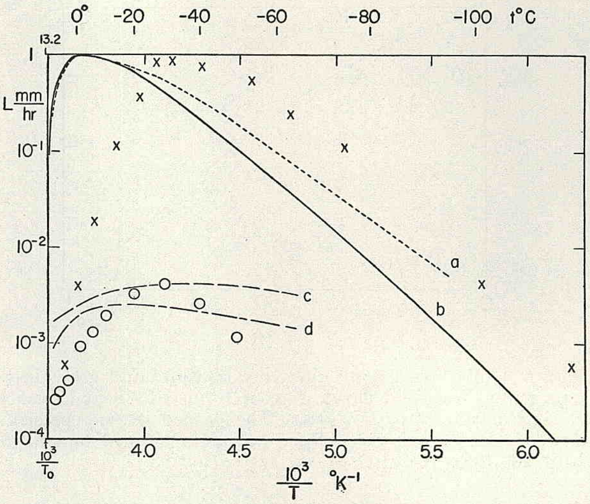

FIG. 8. Comparison of theoretical rate curves with experimental data. $XXXX$, experimental data from Fig. 3; 0000, experimental data of Tammann and Dryer. Calculated curves for $XXXX$ data assuming a one atom complex: For curve b, $\Delta H^*=8.73\times10^3$ cal/mole, $\Delta S^*=8.7$ cal/mole °K, and $A=1.7\times10^{-2}$. For curve a, $\Delta H^*=7.26\times10^3$ cal/mole, $\Delta S^*=7.3$ cal/mole/°K, and $A=7.6\times10^{-4}$. Calculated curves by Cagle and Eyring for 0000 data: Curve c is for a one atom complex; curve d is for an eight atom complex.

This indicates that, although at low temperatures $(1/A)(dA/dT)$ appears to be negligible compared to $\Delta H^*/kT^2$, it is not negligible at higher temperatures. Figure 7 and Eq. (7) also illustrate this point. In order for the theoretical rate curve to fit the experimental data over the whole temperature range, $-(1/A)(dA/dT)$ must continuously increase with temperature (reaching a value 0.51 at 273°K). Qualitatively we expect A to behave in this manner, but before quantitative agreement can be considered satisfactory, A must be evaluated independently. One expects A to be related to the mechanical properties of the white-gray tin interface. A direct experiment to determine the temperature dependence of A is suggested in Sec. IV.

One of the surprising facts concerning the rate of transformation is that L is very sensitive to impurity content, while the temperature at which the maximum rate occurs is relatively insensitive to impurity content. This behavior, illustrated in Fig. 4, is predicted from the preceding theory [see Eq. (12)]. For example, if ΔH^* increases from 8.7×10^3 to 10.0×10^3 cal/mole, L decreases by a factor 30, while T_m increases by only 7°K.

Also shown in Fig. 8 are the experimental rate data of Tammann and Dreyer[19] and corresponding theoretical curves calculated by Cagle and Eyring[30] for a one and eight atom complex as mentioned earlier. The latter authors determine 2600 cal/g-mole as the heat of activation for the white to gray tin transformation, and Dunkerly and Mudge[29] estimate an energy of activation of the order of 180 cal/mole. These discrepancies are

---

[40] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 491. N. F. Mott, Proc. Roy. Soc. (London) **146**, 465 (1934).

discussed in Sec. IV. From Fensham's[41] value of 5900 cal/g-mole for the Arrhenius activation energy for self diffusion in white tin along the a axis, Cagle and Eyring calculate the heat of activation as 5000 cal/g-mole.

One can generalize the present treatment by assuming that several atoms take part simultaneously in the jumps. One can consider, for instance, the case that m white tin atoms and n gray tin atoms react to yield p white tin atoms and q gray tin atoms ($m+n=p+q$; and $n<q$). In the reverse direction r white tin atoms and s gray tin atoms react to yield t white and u gray tin atoms ($r+s=t+u$; and $r<t$). The large number of parameters available to fit the experimental rate data hardly seems to justify this treatment unless the following considerations of the one-atom-jump theory fail to give quantitative agreement. These include quantitative information concerning the temperature dependence of A, ΔH^*, and ΔS^*, recalculation of the bulk white-gray tin free energy difference, and an evaluation of the errors introduced by using *bulk* free energies rather than the free energy for the *reactive* atoms of white and gray tin.

IV. CONCLUSIONS AND COMMENTS

In this paper we have given a survey of the factors influencing the $\beta\rightarrow\alpha$ tin transformation from the standpoint of quality as well as rate of growth. We have shown that it is possible to obtain rather good quality gray tin crystals in the form of bulk samples or thin films. Under favorable conditions of temperature and impurity content, white tin specimens up to 20×2×1 mm have been transformed without cracking. Some of these show single crystal areas about one sq mm, with the largest dimension 2 mm long. Very flat films attached to a substrate have been obtained with an area up to 25×25 mm and thicknesses between 0.0001 and 0.005 mm. Free specimens were as large as 20×10 mm with a thickness of 0.005–0.1 mm. Efforts to obtain gray tin directly by deposition and chemical reactions were unsuccessful; this result remains as yet unexplained.[§§§]

In many publications on the rate of transformation it is difficult to draw conclusions as to the effect of certain parameters because several influences were acting at the same time. Where straightforward conclusions can be reached, results are generally in agreement with our observations. Our investigation, and also other recent work,[21,24] does not seem to support the popular belief that "the factors which increase the speed of transformation will also increase the liability for the transformation to begin."[42] We have already pointed out exceptions to this rule for the case where the samples are mechanically worked or larger size specimens are used.

The best crystals are produced by transformation close to the transition temperature. This can be understood as follows: Fewer strains remain at higher temperatures because of the increased plasticity and larger rate of annealing. Furthermore, ΔG_{wg} approaches zero which results in a higher exchange of atoms from the white and gray tin reactive sites, and thus the growth approaches "equilibrium" conditions.

Mechanical treatment decreases the nucleation time due to an increase in the number of reactive sites. Annealing and oxidation have the reverse effect. These factors have little influence on the linear rate of transformation, because the change in the number of reactive sites is small compared with the number of reactive sites created by the transformation itself.

The influences of sample size and bonding of the sample to a substrate are readily understood when we remember that pressure will slow down the transformation. In smaller crystals the local tensions will be less and the probability of cracking will be reduced.

The effect of impurities on the crystal quality as well as on the rate of growth is difficult to understand. We should realize, of course, that the amount of available data concerning the influence of impurities on quality, nucleation, and linear rate of transformation is still rather limited. At the same time the segregation of the foreign atoms within the crystal as well as the particular phases formed are influenced by the conditions under which the white tin crystals are grown.[23]

One can categorize the impurities in two classes, one which forms mixed crystals, and another favoring solid solutions. A preliminary survey seems to indicate that the former class gives a high linear rate of transformation and good quality crystals, while the latter category seems to have the opposite effect.[‖‖‖] It might be possible that there is some correlation between the existence of mixed crystal regions and the additional strength of the resulting gray tin crystal that is observed.[¶¶¶]

Some investigators[43,44] have attributed the accelerating effects of certain impurities on the rate of transformation to electrolytic action (with moisture present); however, Busch, Wieland, and Zoller[45] have

---

[41] P. J. Fensham, Australian J. Sci. Research A3, 91 (1951).

[§§§] We want to suggest a slightly different approach, namely, the deposition of tin atoms on a cold substrate (gray tin or InSb) at a rate equal to or less than the linear rate of transformation, where sufficient time is allowed for nucleation and growth before the deposition is continued. To our knowledge this method has not been adequately explored, and the latter conditions were not fulfilled in our experiments.

[42] C. E. Homer and H. C. Watkins, Metal Ind. (London) **60**, 364 (1942).

[‖‖‖] An earlier correlation between the rates and the phases by E. Cohen and A. K. W. A. Van Lieshout [Z. physik. Chem. **A178**, 221 (1936)] led to the opposite conclusion.

[¶¶¶] This suggestion has also been made by Groen,[5] in connection with additions of mercury to the tin.

[43] E. Heyn and E. Wetzel, Z. Metallk. 14, 335 (1922).

[44] E. Cohen and W. A. T. Cohen DeMeester, Z. physik. Chem. **184**, 190 (1939).

[45] Busch, Wieland, and Zoller, *Semiconducting Materials* (Butterworths Scientific Publications Ltd., London, 1951), p. 188.

pointed out that this cannot be the sole mechanism responsible for the effect.

Rate theory gives a reasonable picture of the temperature dependence of the linear rate of transformation, however, it might be worthwhile to have a more detailed look at the different parameters which determine L. Considering Eq. (6) and the curve $\ln L$ *vs* $1/T$ of Fig. 8, it is clear that different factors predominate in different temperature regions. At low temperatures the slope approaches a value determined by the heat of activation ΔH^*. The maximum rate occurs at a temperature which depends on T_0, ΔH^*, and $(1/A)(dA/dT)$. Finally, at high temperatures the shape of the rate curve is influenced chiefly by the temperature dependence of ΔG_{wg} and $(1/A)(dA/dT)$.

From these considerations one can readily see that when impurities were added to the white tin (Fig. 4), ΔH^* changed only slightly, while ΔG_{wg} or $(1/A)(dA/dT)$ were more sensitive to impurity content. The small value of the heat of activation calculated by Cagle and Eyring[30] compared to that derived from our work is also apparent. In Fig. 8 the two sets of experimental rate data show approximately the same temperature dependence, particularly at low temperatures. One should remember that we have fitted the slope of the theoretical rate curve to that of the experimental data at *low temperatures only*, and thus obtained ΔH^*; the discrepancy at higher temperatures was attributed to possible errors in ΔG_{wg} and to an increase of $(1/A)(dA/dT)$ which was not included in the theoretical curve shown in Fig. 8. On the other hand, Cagle and Eyring have varied the parameters in their theory to obtain the best fit over the *whole* temperature range. The slopes of their theoretical curves at low temperatures are much less than indicated by the experimental data. The energy of activation for the white to gray tin reaction was estimated by Dunkerly and Mudge[29] from volume rate of transformation studies at relatively high temperatures, and was interpreted in terms of a considerably different theory.

It might be possible to obtain information concerning the temperature dependence of A or $(1/A)(dA/dT)$ by determining the nucleation time in hot and cold work experiments. One could subject samples of white tin to a fixed amount of mechanical treatment at various temperatures and measure the nucleation time (t_n) at one particular temperature (T_n). An additional experiment with T_n as the parameter would allow a determination of the relative number of reactive sites created and their rate of annealing. Reactive sites are created by the white to gray tin transformation as well as by mechanical working. Thus A, being the fraction of reactive atoms at the white-gray tin interface, will be directly related to the nucleation times determined in the mechanical work experiments.

The various forms of gray tin crystals should be useful for further determinations of the electrical and optical properties, and their applications. The existing knowledge of the factors affecting the transformation are sufficient to minimize or prevent the growth of gray tin when this is desired. Finally, electrical and rate of transformation data can be used as a supplementary analysis of impurities in tin.****

ACKNOWLEDGMENTS

The author is indebted to Dr. R. G. Breckenridge for suggesting the problem and for constant advice and encouragement. Thanks are also due Professor R. L. Sproull for his continued interest. Discussions with Dr. L. M. Brown and Dr. B. Ransil concerning the rate theory were helpful. The author wishes to acknowledge the assistance of Miss E. E. Seitz with the chemical and electrodeposition experiments, and the help of Mr. S. Platnik with the cold work measurements. He is indebted to Mr. J. M. Smith and Mr. W. J. McKean for construction of apparatus. Discussions with all the members of the Solid State Physics Section and a critical review of the manuscript by Dr. E. S. Hedges and Dr. H. P. R. Frederikse have been beneficial.

**** *Note added in proof.*—Large single crystals of gray tin with well-developed crystallographic planes have been grown from a tin-mercury amalgam [O. N. Tufte and A. N. Ewald, Bull. Am. Phys. Soc. Ser. II, **3**, 128 (1958)]. Burgers and his co-workers have summarized the results of their investigations on the mechanisms and kinetics of the allotropic transformation of tin [W. G. Burgers and L. J. Groen, Discussions Faraday Soc. No. 23, 183 (1957)].