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SINGLE CRYSTALS OF "GLOBULAR MOLECULES" FROM THE MELT

By

Charles A. Aeby

A Thesis
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Physics

The University of New Mexico
1964

This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

A. Rosenzweig
Dean

May 25, 1964
Date

SINGLE CRYSTALS OF "GLOBULAR MOLECULES" FROM THE MELT

By

Charles A. Aeby

Thesis committee

John R. Green
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TABLE OF CONTENTS

Page

LIST OF ILLUSTRATIONS iii

INTRODUCTION 1

Chapter

I. THEORY OF GROWTH FROM THE MELT 2

II. METHODS 5

III. PROPERTIES OF PLASTIC CRYSTALS AND COMPOUNDS USED 9

IV. EXPERIMENTAL APPARATUS 13

V. EXPERIMENTAL RESULTS 19

VI. IDENTIFICATION AS SINGLE CRYSTALS 29

VII. CONCLUSIONS 33

ACKNOWLEDGMENTS 35

LIST OF REFERENCES 36

LIST OF ILLUSTRATIONS

Figure Page

1. Upper Section 14
2. Lower Section 15
3. Lowering Mechanism 17
4. Temperature Gradient for dl-Camphene; run 1 . . 20
5. Temperature Gradient for dl-Camphene; run 2 . . 21
6. Temperature Gradient for dl-Camphene; run 3 . . 23
7. Temperature Gradient for dl-Camphene; run 4 . . 24
8. Temperature Gradient for d-Camphor 26

INTRODUCTION

This thesis is an investigation of the possibility of growing single crystals of dl-camphene, d-camphor, and cyclohexanol. These are organic compounds, characterized by "globular molecules", which form plastic crystals immediately below their melting point. Single crystals were desired in order to study, by ultra-sound techniques, properties pertinent to the evaluation of the elastic constants of these crystals. Primary emphasis was placed on growing crystals of dl-camphene, since it is conveniently handled at room temperatures.

Methods of growth from the melt were chosen because of the relatively fast growth rates, compared to vapor or solution techniques. Secondary considerations were simplicity of the apparatus and the final geometry of the crystals, with the cylindrical shape being well suited for the ultrasonic measurements.

CHAPTER I

THEORY OF GROWTH FROM THE MELT

The growth of crystals from the melt may be considered in two distinct steps. [1] First, there must be formation of a nucleus or "primary cell" of the crystal, the smallest structure capable of sustaining further growth. Second, the subsequent growth of this nucleus must be considered.

In the liquid state the temperature of the melt will be everywhere greater than the melting point if there is no supercooling. In this condition the molecules will be in a state of random thermal motion, with the possibility that the proper number of molecules will collide in the configuration characteristic of the crystal's primary cell. The energy binding these molecules determines whether they remain in the crystal configuration or are dissociated by the thermal energy. In the simplest case, the molecules will separate if the temperature is high enough. At the melting point, it would appear that the nucleus would have an equal chance of surviving and could then continue to grow; however, this is not the case. Consider a macroscopic crystal surface and let <u>C</u> represent the cohesive force holding a given molecule in place. Also let <u>L</u> represent the forces between the liquid and the crystal surface, and <u>D</u> the forces tending to disintegrate

the crystal. The latter forces are due to thermal agitation, and are dependent on the temperature of the melt. In this case the crystal would be able to hold the molecule at a temperature infinitesimally below that for which

$$(C-L)=D. \qquad (1)$$

This implies the crystal can then continue to grow by the addition of other molecules, providing the energy liberated (latent heat of crystallization, numerically equal to the latent heat of fusion) can be absorbed either by the crystal itself or the surrounding melt.

In comparison consider a nucleus just formed in the melt. A given molecule in this nucleus will necessarily be bound by a smaller force than would a similar molecule in a macroscopic crystal. Therefore $\underline{C}$ will be smaller than in the previous case, since it is held by fewer immediate neighbors, and consequently at the melting point the probability of disaggregation exceeds that of aggregation. Under these circumstances the nucleus cannot exist long enough to acquire additional molecules by collision and will not grow. It is therefore necessary that the melt be supercooled slightly below the freezing point in order to decrease $\underline{D}$ so that the nucleus can exist long enough to acquire additional molecules. Growth nuclei are not formed simultaneously throughout the melt. As a result, each nucleus formed acts as a separate seed, growing independently of the others and competing, until contact, for the remaining melt.[2] The solid thus formed will be a poly-

crystal, as is generally the case with normal cooling.

In order to obtain a single crystal, a means of isolating a growing nucleus must be established and its growth from the melt must be regulated. The rate of growth is determined by the rate at which the latent heat of crystallization can be removed from the solid/melt interface either by conduction through the crystal to some heat sink or by absorption in the slightly supercooled melt near the interface. The latter condition is to be avoided, since the growth is then too rapid and not easily controlled.[3]

CHAPTER II

METHODS

Only two of the several methods available will be discussed. They are the Bridgman and the Stockbarger methods.[4] In the Bridgman method the melt is confined in a sealed cylindrical crucible, tapered to a capillary at one end. A constriction in the capillary is often used. The crucible and melt are slowly lowered from above through a furnace which maintains a temperature gradient passing through the freezing point of the melt. The crucible is started in a region where the temperature is greater than the melting point and is lowered into a cooler region. The tip of the crucible with the constricted capillary enters the freezing plane first. This permits the formation of one or more nuclei which will then grow from the melt. Even if a number of nuclei are formed, the one growing most rapidly in the upward direction will suppress or crowd out the others at the constriction. Beyond the constriction the surviving crystal continues to grow uniformly through the remainder of the melt; thus a single crystal is formed. In the Bridgman technique, all of the heat of crystallization must be lost to the crucible; this requires that the heat flow radially from the center of the crystal. The outer regions

of the crystal cool first, with the solidification continuing toward the cylinder axis. This leads to a scarcity of melt in the center which in extreme cases produces a large shrinkage hole in the center of the crystal. The possibility also exists that additional growth nuclei can form at the outer periphery to create a polycrystalline ingot. Hence, the Bridgman technique does not always result in single crystals even with very slow lowering rates.

Stockbarger's method introduces two major modifications while retaining the principal of lowering the melt through a temperature gradient. First, the tapered crucible is replaced by one having a conical bottom. In such a crucible the selectivity of the capillary and constriction are eliminated. Therefore some other mechanism must determine which of the growth nuclei formed will dominate. This mechanism is most probably associated with one orientation of the nucleus, with respect to the direction of heat loss, being more favorable to rapid growth.[5] It is hoped that one nucleus will dominate quite early; this results once again in a single crystal, except perhaps for a small region confined to the tip of the crucible.

Second, the sample is supported from below by a crucible holder mounted on a metal rod, the rod passing through the bottom of the furnace. The rod and holder act as a heat sink; and, under the proper balance of temperature gradient and lowering rate, the latent heat of crystallization is

removed vertically downward more rapidly than by radial conduction. This minimizes the extent of the shrinkage hole and confines it to a concave depression at the top of the crystal. This depression can be made negligible, and the chances of the formation of unwanted growth nuclei can be eliminated by a later refinement to the Stockbarger technique. This refinement provides a means of controlling the shape of the isotherm defining the solid/melt interface.[6] In the original Bridgman furnace this isotherm was always concave upwards. By the addition of an auxillary heater at the diaphragm, separating the upper and lower sections of the furnace, the isotherm can be made concave upwards, planar, or convex, depending on the ratio of the power inputs to the diaphragm heater and the furnace core. The less concave the interface, the less favorable are the conditions for forming spurious nuclei.[7]

In addition to the importance of maintaining the proper temperature gradient, two other factors must be considered: (1) the rate at which the crucible is lowered through the furnace, and (2) the elimination of mechanical disturbances.

The rate of lowering is necessarily limited by the rate at which the latent heat of crystallization can be conducted away from the solid/melt interface. This, in a sense, defines the rate of growth in a particular system. As might be expected, the Stockbarger method allows faster rates than does the Bridgman technique, since the crucible holder and lowering

rod act as additional heat sinks. As a general rule, conditions are more favorable for growth of single crystals at very slow rates. The reason for this is that as much time as possible should be allowed for the new molecules striking the interface properly to align themselves in the crystal lattice. The effect is to establish a steady state condition for growth.

Isolation of the system from mechanical shock and vibration is essential, as any such disturbance will disrupt the orderly growth process.

CHAPTER III

PROPERTIES OF PLASTIC CRYSTALS AND COMPOUNDS USED

At this point some of the distinguishing characteristics of plastic crystals should be pointed out.[8] 1) upon freezing, almost all globular molecules, including the three discussed herein, crystallize in a cubic structure. 2) even in the crystalline form the molecules appear to possess rotational freedom that is not a great deal less than they have in the liquid state. The internal resistance to this rotation increases as the temperature decreases. Because of the asymmetrical form or shape of the molecules and the fact that they are rotating, they occupy a greater volume than if they were non-rotational.[9] As a consequence they are easily deformed and hence the term "plastic crystal." 3) as the temperature of the plastic crystals is lowered, a point is reached where they undergo a solid/solid transition. This transition results in a change to a crystal structure of lower symmetry and may or may not be accompanied by a complete loss of rotational freedom. 4) the entropy of fusion, i.e., the heat of fusion divided by the temperature at the melting point, is relatively small for plastic crystals, generally less than 5 cal deg^{-1} mol^{-1}.

The compounds used for crystallization were dl-camphene, d-camphor, and cyclohexanol. Their properties are listed in Table I. [8,10,11]

Purification and preparation of the materials required varying techniques. The camphene was redistilled up to three times from Eastman-Kodak practical grade. The melting point acheived in this manner was 49.5°C. The crucibles were filled with melted camphene and sealed with an inert teflon stopper. Camphor was prepared from Eastman-Kodak practical grade by a sublimation-recrystallization process. The camphor was placed in a vertical drying column and was sublimed by a constant flow of hot dry air. The air was dried by circulation through a vertical drying column containing a silica dessicant and heated by a coil of nichrome wire wrapped about the outside. The camphor vapor was then circulated through a primary condenser and two smaller secondary condensers immersed in an ice-bath to produce recrystallization. The condensers were removed and the purified camphor taken out in powder form. A melting point of 175°C was obtained with a yield of approximately 65%. The process is indicated in the accompanying block diagram. Purified camphor was placed in the crucibles in powder form and compacted with a glass stirring rod. A teflon plug was used to seal the crucible and an epoxy resin cap was applied to close the system.

Cyclohexanol was prepared by refluxing over burnt lime

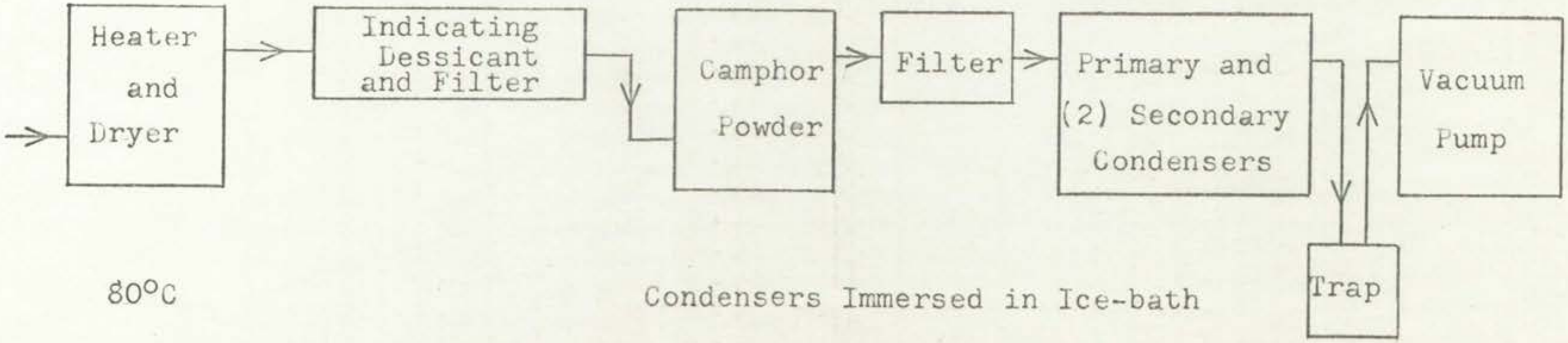
TABLE I

PROPERTIES OF PLASTIC CRYSTALS

Compound	Formula	Mol. Wt.	Index of Refrac.	Density gm/cm^3	Melting Pt. °C	Boiling Pt. °C	Trans. Temp. °C	Crystal Structure	
								I	II
dl-camphene	$C_{10}H_{16}$	136.23	1.4402	0.879	50	159	-118	bcc	----
d-camphor	$C_{10}H_{16}O$	152.23	1.532	0.990	176	204	97	fcc	rhomb.
cyclohexanol	$C_6H_{11}OH$	100.63	1.46560	0.962	22-25	161.5	-10	cubic	----

BLOCK DIAGRAM

SUBLIMATION-RECRYSTALLIZATION OF d-CAMPHOR



80°C

Condensers Immersed in Ice-bath

and fractional distillation.[12] A second fractional distillation to remove remaining water impurities was made from a flask containing metallic sodium. The melting point of the cyclohexanol was 24°C. To fill the crucible, the cyclohexanol was melted and a hypodermic syringe used to transfer the material. Sealing was done with a teflon stopper.

CHAPTER IV

EXPERIMENTAL APPARATUS

The design of the furnace and lowering mechanism facilitates use in both the Bridgman and Stockbarger methods. The upper section of the furnace (Fig. 1) consists of an inner core (A) of Vycor tubing. A length of #22 nichrome wire (B) wrapped the length of the tube in three equal sections supplies the heat. The turns ratio from top to bottom is 4:1:2. To prevent the turns from slipping together as a result of thermal expansion, an epoxy resin is used to cement the wire to the tube. The inner core is centered and supported at the bottom by a grooved masonite rim (C). The upper end is positioned by a similar rim (D). A metal sleeve (E) encases the core and support rims, with the space between the sleeve and the core filled with sand for insulation. The diaphragm heater (F) is made of a ring of coiled nichrome wire placed at the bottom of the core. It is supported above a metallic heat baffle (G) centered in the tube. Power is supplied to the core and diaphragm heaters through connectors (H) from separate Variac autotransformers. The current to each heater is measured.

The lower section (Fig. 2) consists of an inner core (A) of copper tubing. This core is centered in a metal

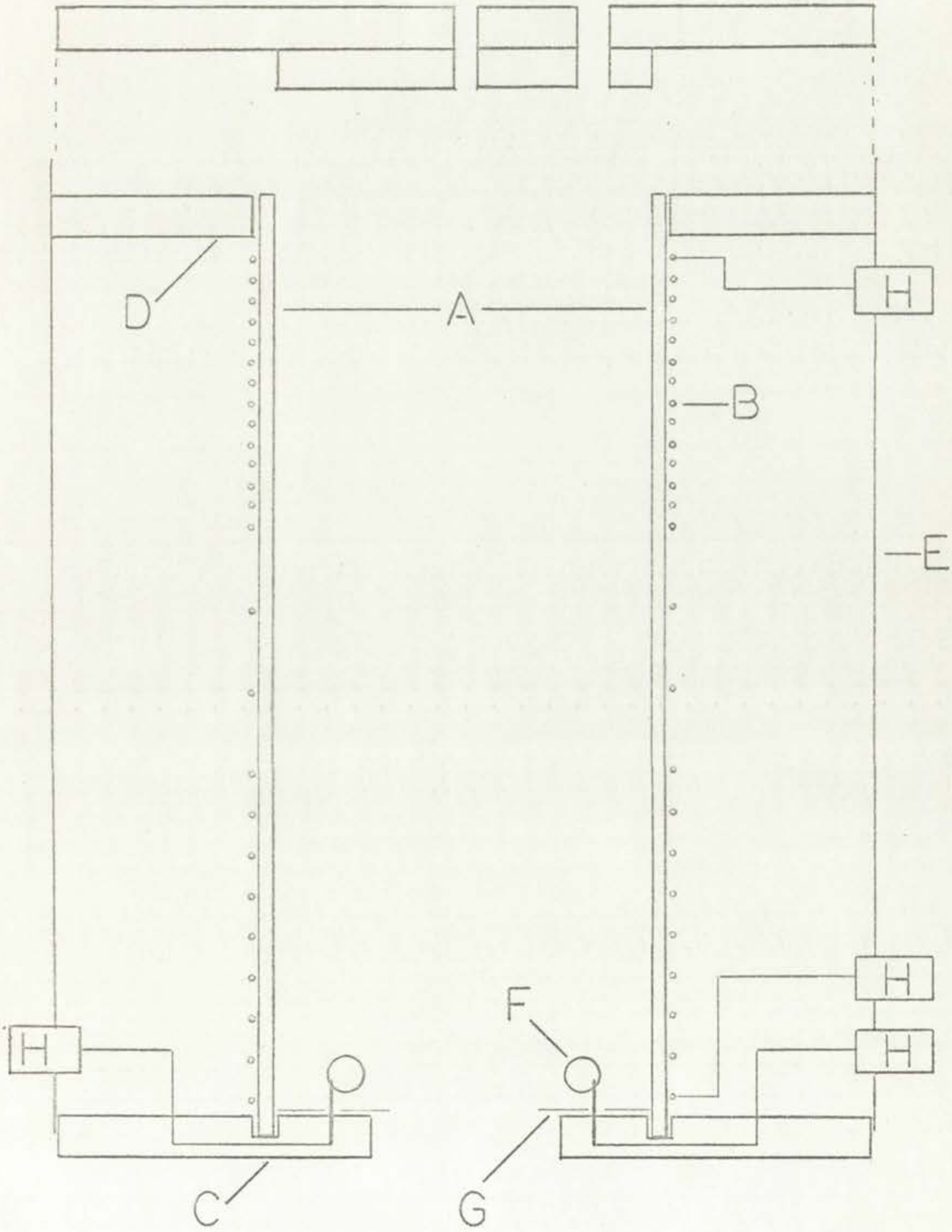


FIG. 1

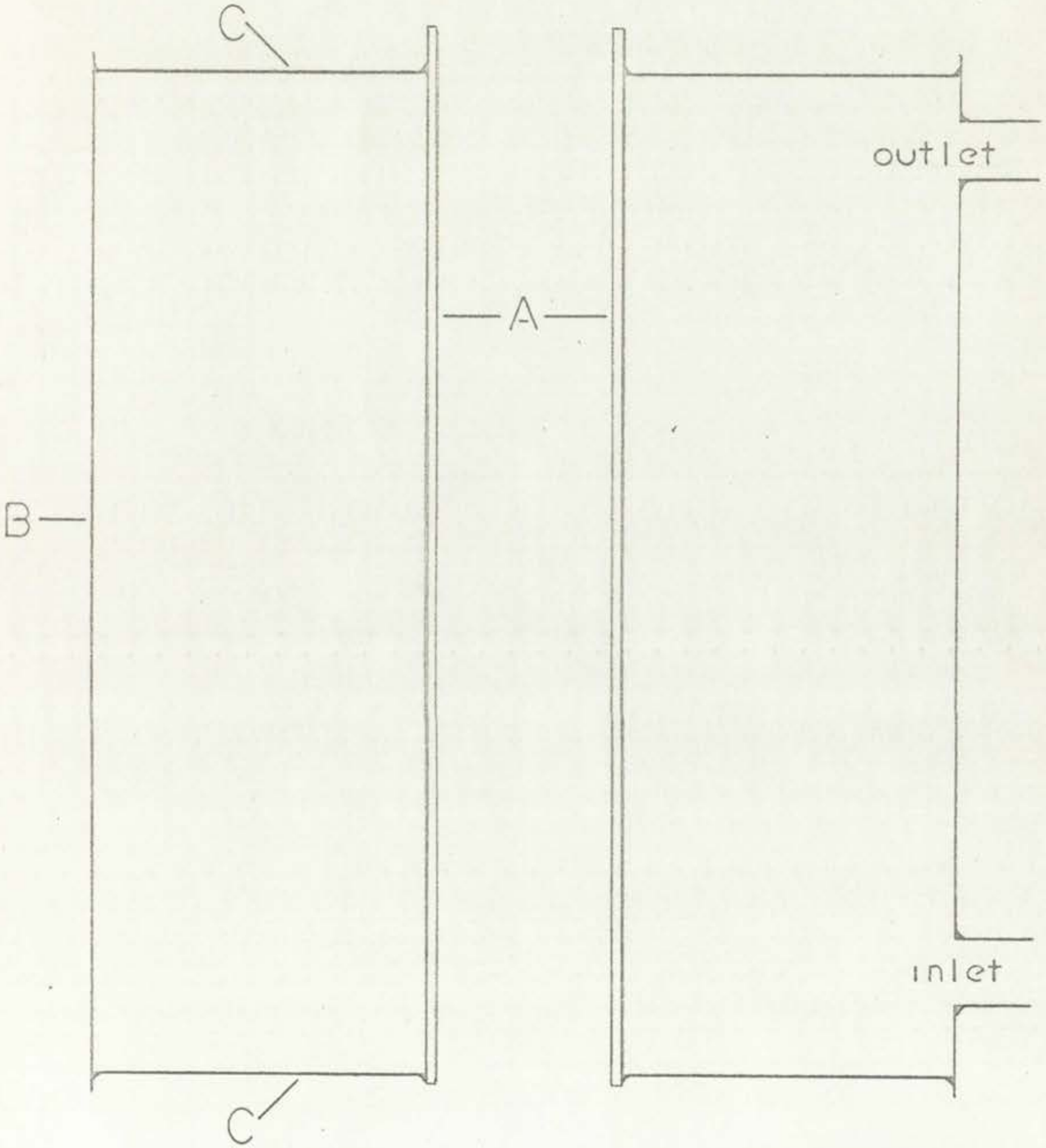


FIG. 2

sleeve (B), by two metal rims (C). The rims are soldered to the core and the sleeve to form a water jacket with inlet and outlet. The copper tube extends into the upper section, below the baffle, to align the two sections.

The lowering mechanism (Fig. 3) consists of two aluminum platforms separated by two rods 1 ft. in length. The upper platform (A) supports the furnace and centers it by means of a masonite disk (B). The platform also holds the teflon guide (C) and the fixed pulley (D). The lower platform (E) holds the motor mount with the motor (F), the spindle (G), and microswitch (H). Rubber washers (I) separate the motor mount and lower platform to eliminate transmission of motor vibrations. Two 115 volt synchronous motors of 1/60 rpm and 1/180 rpm can be used interchangeably with various spindles to change the lowering rate. The microswitch is situated so as to shut off the motor when the crystal has completed its pass. The entire lowering mechanism can be mounted on the laboratory wall; and by inverting the mechanism and suspending the furnace sections below, one can convert from the Stockbarger to the Bridgman method.

The lowering rod (J) is a length of 1/4-in. diameter stainless steel, which presents a minimum of friction with the teflon guide. A pulley (K) is attached to the end of the rod passing through the bottom of the lower section. The rod is lowered by a string fixed at one end to the upper platform, passing under the lowering rod pulley, over the

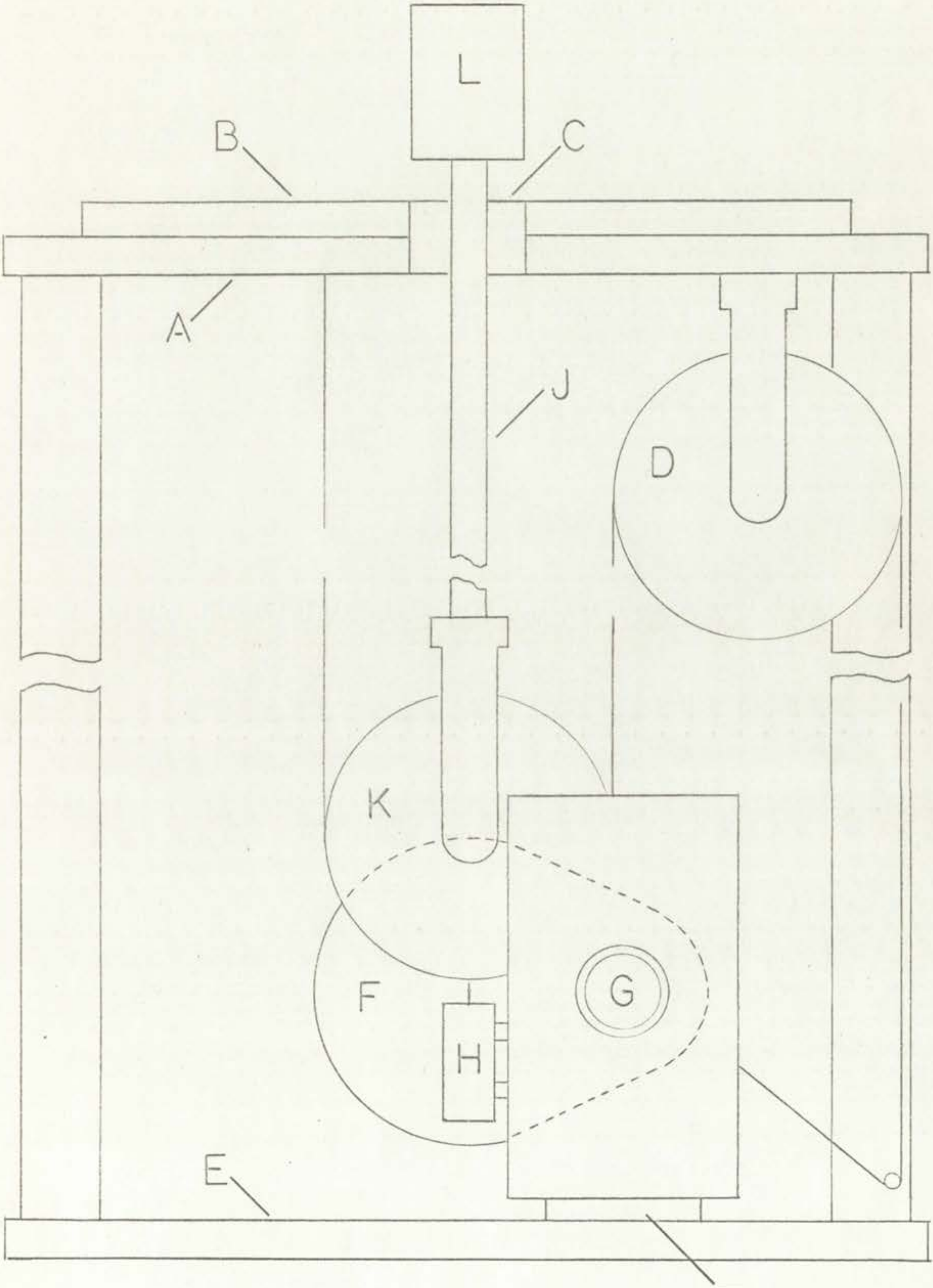


FIG. 3

stationary pulley, down through a guide on the lower platform, and wrapped about the spindle. The crucible holder (L) is made of teflon and slips onto the top of the lowering rod. A conical hole in the top of the teflon holds the crucible. The crucibles are drawn from 7/16-in. diameter Pyrex or glass tubing, in lengths from 1 1/2 in. to 3 inches.

Data for the temperature gradient curves are obtained with a thermocouple in conjunction with a Leeds and Northrup Model 8686 millivolt potentiometer. The junction is lowered through the furnace in 1-cm. increments and the temperature plotted as a function of distance from the top.

CHAPTER V

EXPERIMENTAL RESULTS

Initially it might be illuminating to illustrate the effects of various temperature gradients, rate changes, and the use of the additional diaphragm heater in the Stockbarger furnace. As a matter of convenience, most of the experimentation was done with camphene. Some of the more interesting runs are noted.

CAMPHENE

The first run was made through the gradient indicated (Fig. 4), and the result is shown in the sketch. The sample was free from inclusions for approximately the first centimeter from the tip. The beginning of the shrinkage hole started about 7 mm. from the bottom. A small air bubble appeared about half way up the sample, with the upper 1 3/4 cm. heavily striated. The striations are parallel lines or planes of minute vacancies with the same appearance as the small trapped air bubbles in ice cubes, which are essentially water crystals grown from the melt. As indicated, the diaphragm was unheated and the lower core was not cooled.

The temperature gradient through the melting point was steepened (Fig. 5) by cooling the lower core with

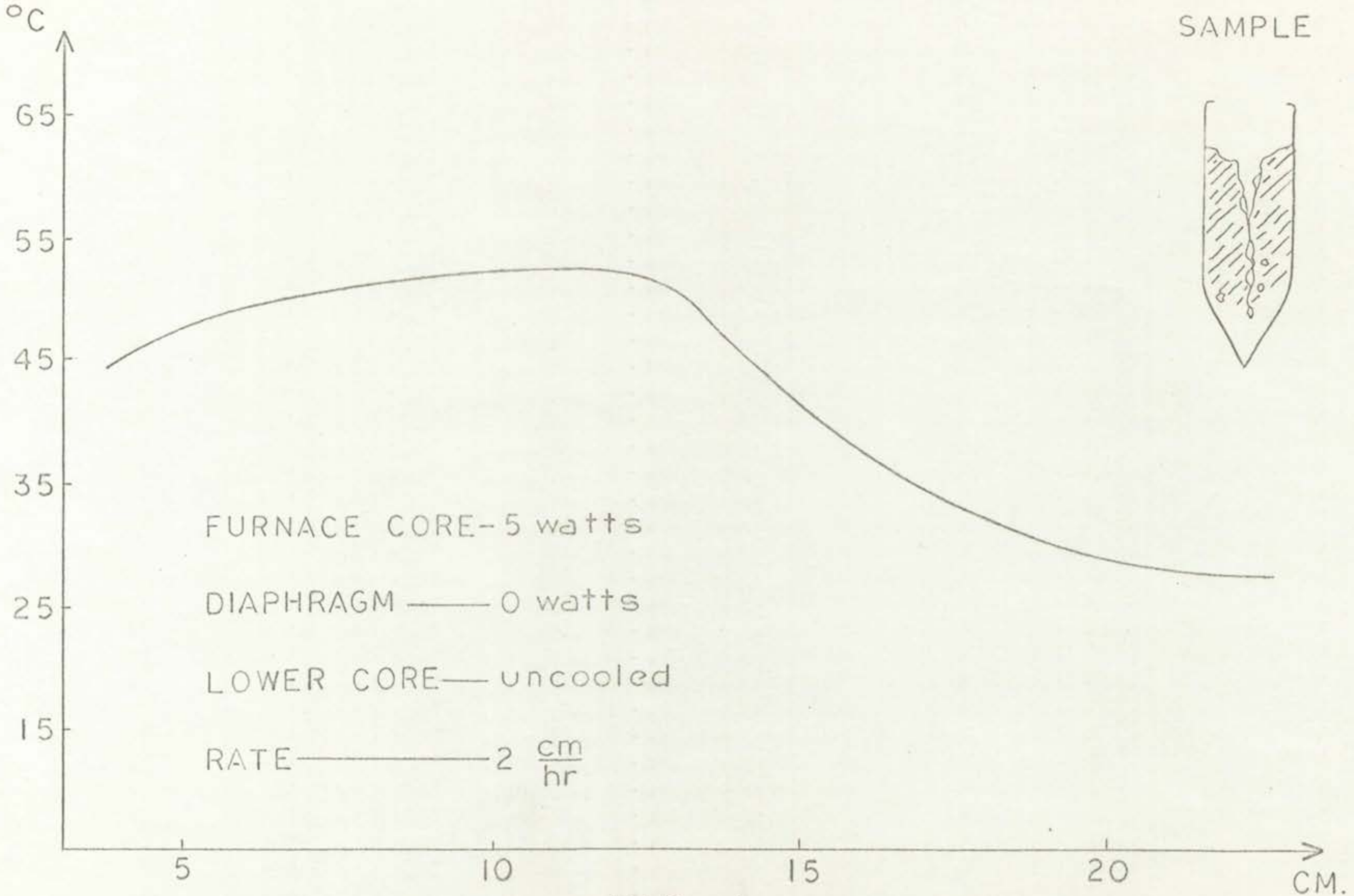

°C
65
55
45
35
25
15
5
10
15
20
CM.
SAMPLE
FURNACE CORE- 5 watts
DIAPHRAGM —— 0 watts
LOWER CORE— uncooled
RATE —— 2 $\frac{cm}{hr}$

FIG. 4

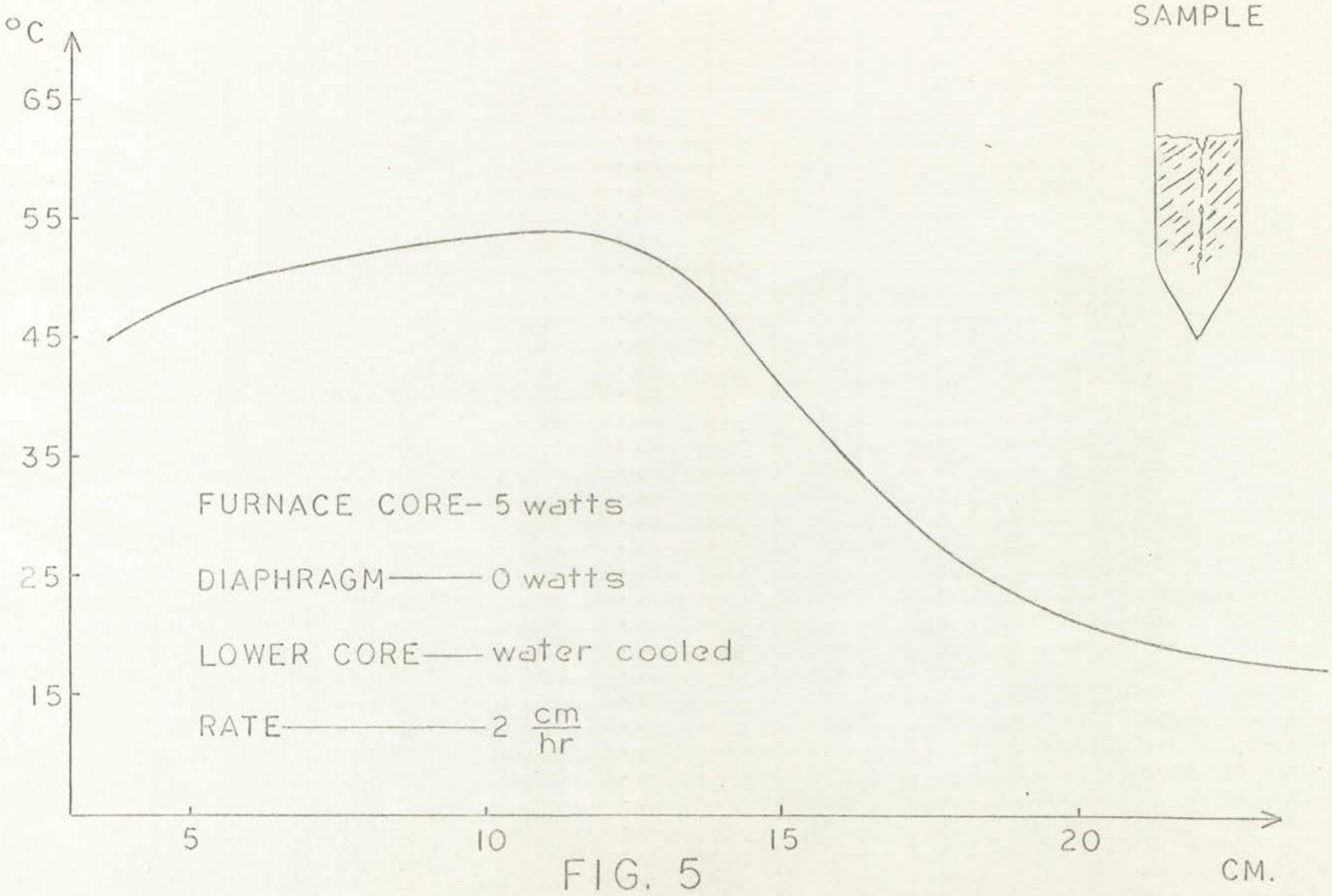

°C
65
55
45
35
25
15
5
10
15
20
CM.
SAMPLE
FURNACE CORE- 5 watts
DIAPHRAGM——— 0 watts
LOWER CORE—— water cooled
RATE————— 2 $\frac{cm}{hr}$

FIG. 5

circulating tap water. The diaphragm was still unheated. No bubbles appeared and the striations were contained in the last 1 1/2 cm. of the sample. Although the shrinkage hole started near the same point, the extent at the top of the sample was much less.

For the next run, (Fig. 6), power was supplied to the diaphragm heater, with the same input in the upper core and with cooling in the lower core. The striations appeared only in the upper centimeter of the sample with no bubbles evident. The shrinkage hole was absent, save for a slight concave depression on the upper surface. It should be noted that for these first trials there were three minor differences in the furnace construction from the final form shown in Chapter IV: (1) the upper section was not insulated, (2) the inner core windings were reversed, i.e., more dense at the bottom than at the top, and (3) an aluminum crucible holder was used in place of the teflon. All subsequent runs were made with the final configuration.

The lowering rates were decreased from 2 cm/hr to 1/3 cm/hr. At intermediate rates the striated region decreased in extent and virtually disappeared with a rate of 2/3 cm/hr. The temperature gradient was unchanged for these trials. With the rate decreased to 1/3 cm/hr, as shown in Fig. 7, the resulting crystal was completely transparent. There was no evidence of the shrinkage hole or crystal boundaries, and no striations could be seen. It is interesting to note the

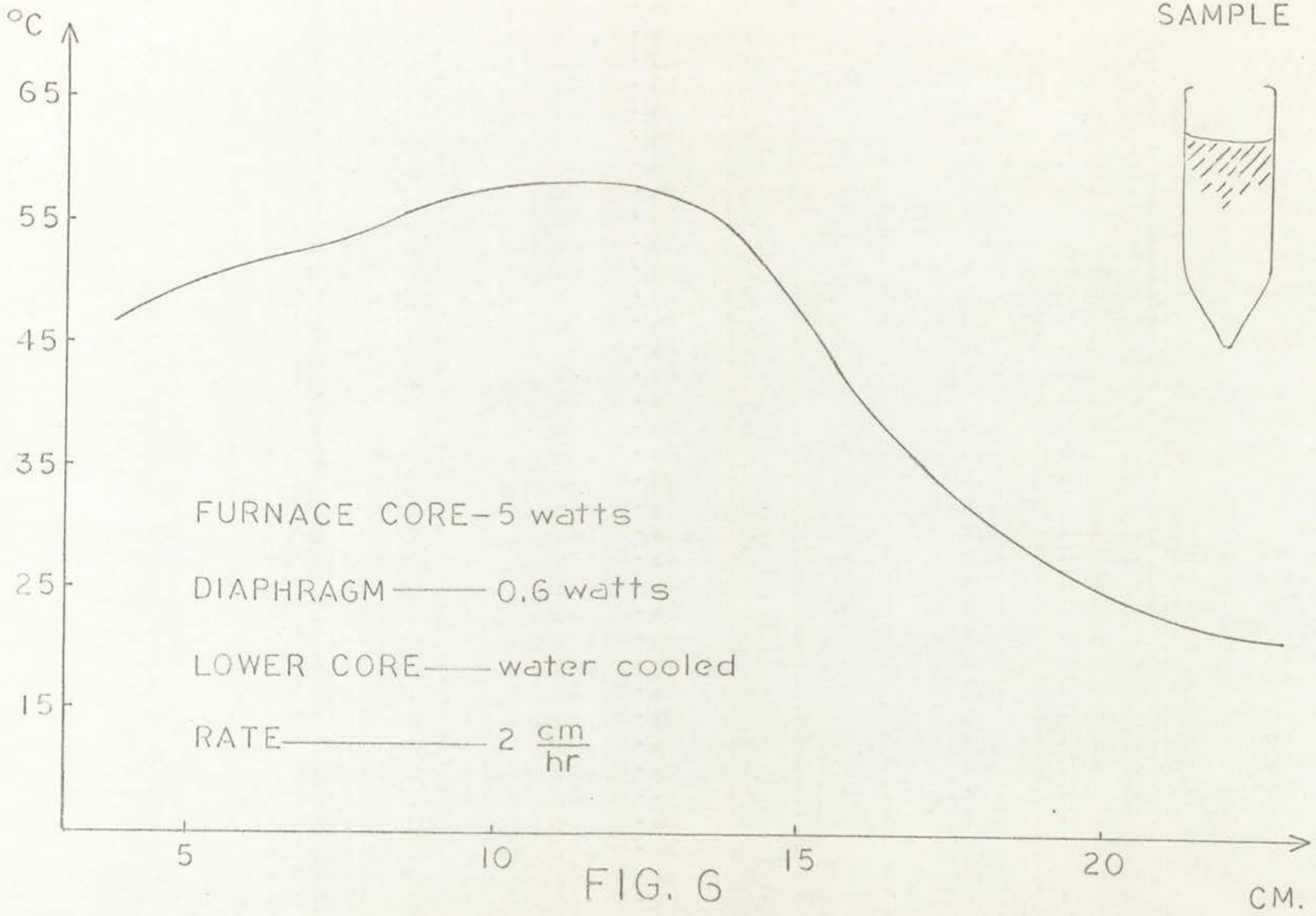

°C
65
55
45
35
25
15
5
10
15
20
CM.
SAMPLE
FURNACE CORE—5 watts
DIAPHRAGM——— 0.6 watts
LOWER CORE——water cooled
RATE————— 2 $\frac{cm}{hr}$

FIG. 6

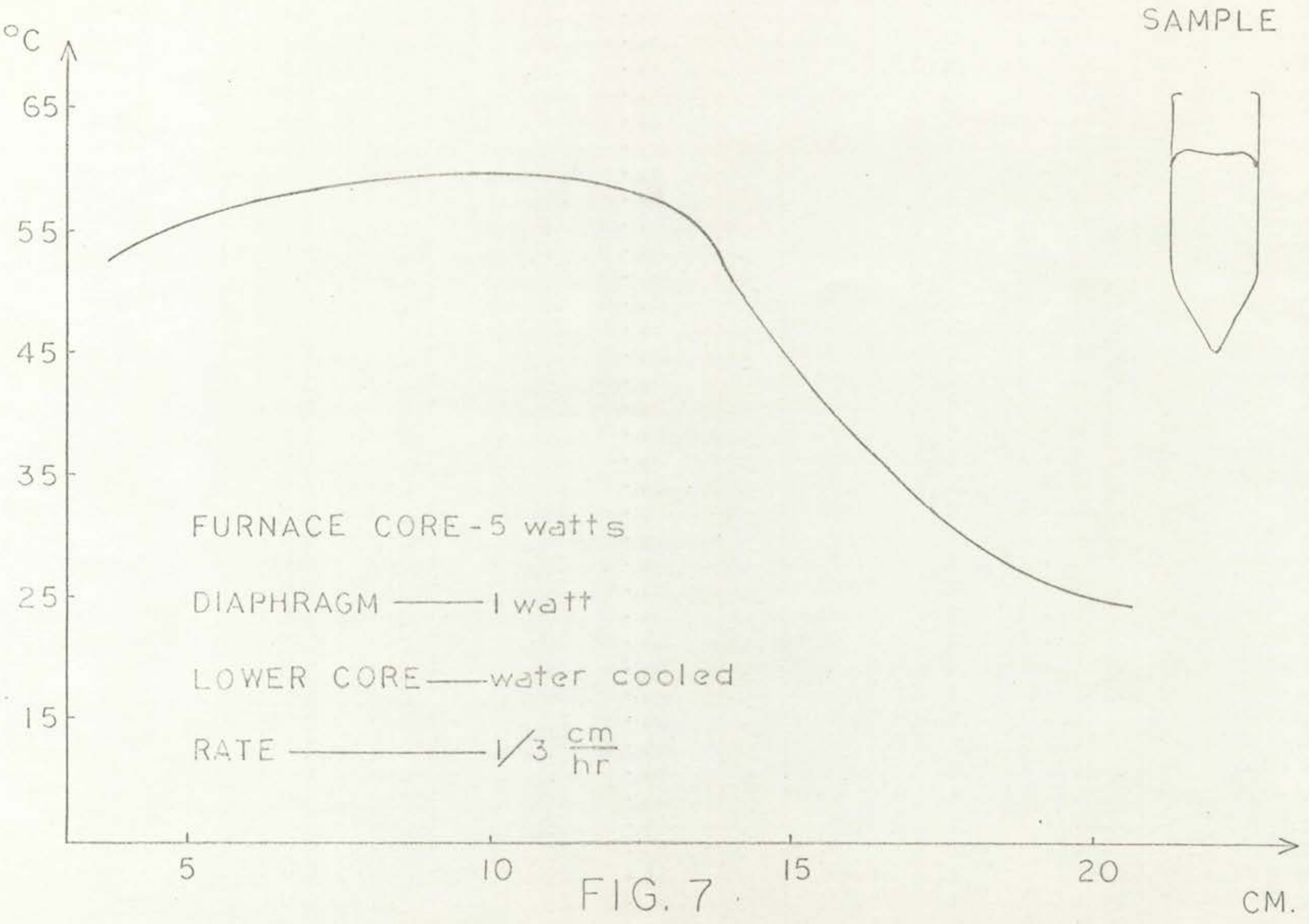

°C
65
55
45
35
25
15
5
10
15
20
CM.
SAMPLE
FURNACE CORE - 5 watts
DIAPHRAGM ——— I watt
LOWER CORE —— water cooled
RATE ——— 1/3 cm/hr

FIG. 7

progression of the contour of the upper surface of the crystals, as the combination of the diaphragm heater and the heat loss through the crucible holder and support rod, coupled with the lower rate, minimized the depression.

CAMPHOR

Several combinations of power input were tried to establish a gradient suitable for growing camphor crystals. The conditions shown in Fig. 8 gave consistent results. However, single crystals of camphor stable at room temperature cannot be expected from this method, since the first solid/solid transition occurs at approximately 97°C. In order to study the cubic phase of the crystal sample, the lower section was replaced by an oil bath maintained at a temperature 10°C above the transition point. The lowering mechanism was inverted and the sample lowered from above as in Bridgman's technique. With the sample suspended in the oil bath, plane polarized light was passed through it and an analyzer used to detect any rotation. No rotation was noted and the completely transparent sample showed little or no internal scattering.

The crucible was then removed from the bath and allowed to cool below the transition point. The sample was placed between crossed polaroids, and the onset of the transition was evidenced by very small regions where the light could no longer be extinguished. These regions grew until the entire crystal had undergone the transition to the rhombic

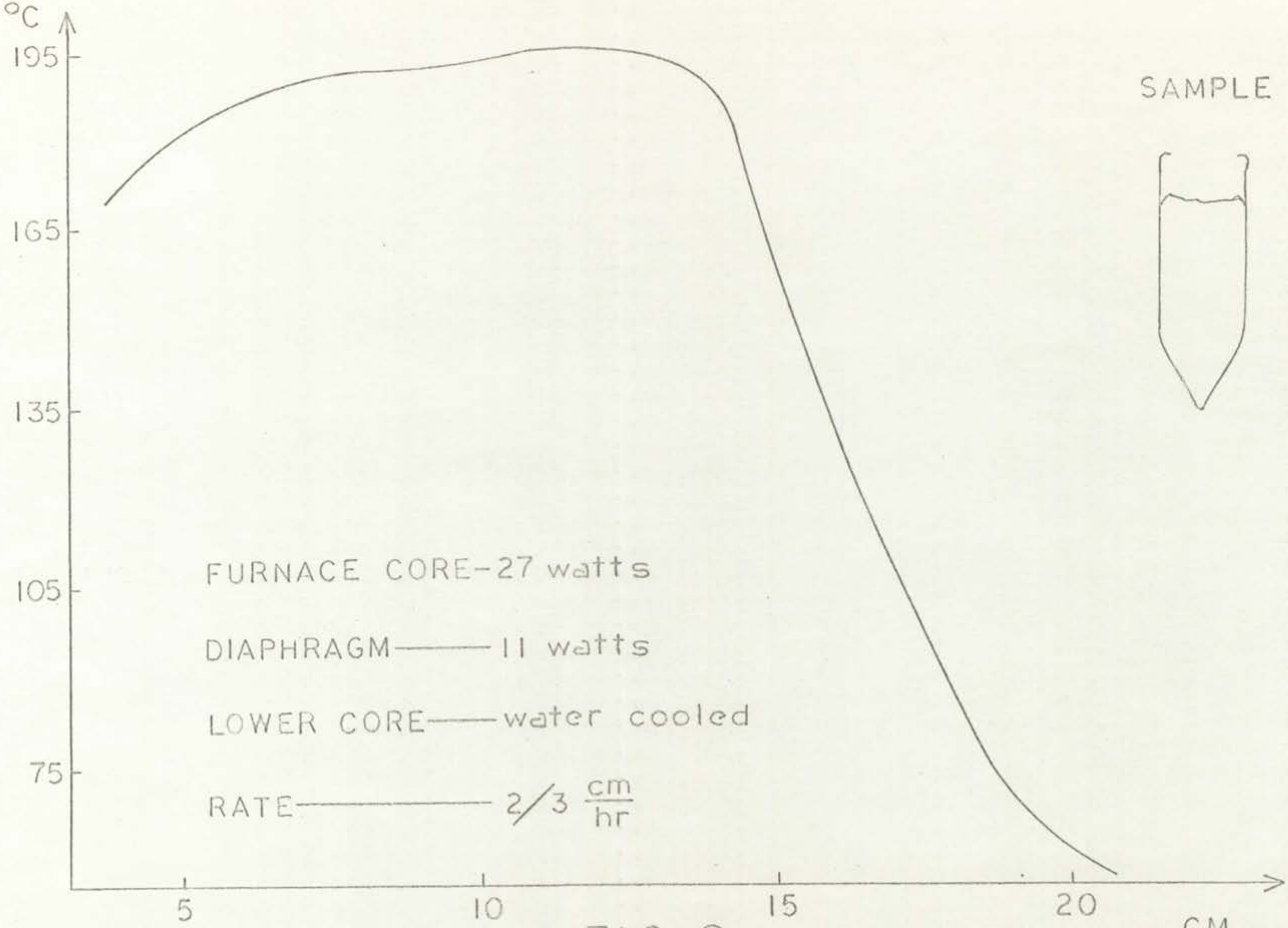

°C
195
165
135
105
75
5
10
15
20
CM.
SAMPLE
FURNACE CORE-27 watts
DIAPHRAGM——11 watts
LOWER CORE——water cooled
RATE——2/3 cm/hr

FIG. 8

or hexagonal phase. The resulting polycrystalline ingot destroyed the polarization. The sample was re-heated above the transition point and its transparency regained. Again using the polaroids, it was found that the light could be extinguished except for a certain amount of internal scattering that was not present before the first transition. Unsuccessful attempts were made to quench a crystal to keep it in its cubic form at room temperature. The crystal could not supercool to the extent needed, and the transition occured almost immediately. Thermal contraction shattered the sample.

The values given in the literature for the solid/solid transition in camphor range between 90°C and 107°C. The 97°C value was determined using a sample cell 1 mm thick, filled with camphor and placed in an environmental chamber between crossed polaroids. The temperature in the chamber was lowered from 110°C in 2° increments, the sample attaining thermal equilibrium at each setting. The temperature was monitored with a thermocouple. The onset of the transition occured at 97°C. When the sample was warmed through the transition, a value of 100°C was obtained.

CYCLOHEXANOL

The apparatus was used in the Bridgman manner in the attempts to grow crystals of cyclohexanol. A test tube immersed in an ice-water bath replaced the lower water jacket. The bath was insulated by a styrofoam box and only

the diaphragm heater was supplied with power, as this was sufficient to keep the sample melted in the upper core. Results obtained with the cyclohexanol were inconsistent. A completely transparent sample was never obtained. A slower lowering rate and a more efficient method to force cooling of the lower section would probably prove beneficial.

CHAPTER VI

IDENTIFICATION AS SINGLE CRYSTALS

The grown samples were tentatively identified as single crystals by comparing their mechanical and optical characteristics with polycrystalline samples of the same compounds. The polycrystal samples were pressed disks approximately 1/2 inch thick and 5/8 inch in diameter. Comparisons were also made with samples allowed to cool naturally from the melt.

CAMPHENE

In the investigation of the mechanical properties of the grown crystals, the crucible plug was removed and the conical section cut through with a glass saw. The crystal could then be pushed out of the tube. Grown samples of camphene exhibited a marked difference in mechanical strength and cohesiveness, as compared to the pressed disks. The disks could not support even slight pressures without crumbling. The smaller constituent crystals, which had made up the disks, exhibited well-defined faces making up the boundaries. These smaller crystals could not be further subdivided. Applied pressure merely deformed them until their internal binding was overcome and the sample was crushed. The individual crystals obtained when the pressed disks were

broken up were transparent and remained so after being somewhat deformed. These crystals also exhibited the waxiness characteristic of plastic crystals. The grown crystals possessed all the characteristics of the smaller single crystals comprising the pressed disks. Pressure served only to deform the sample with no crumbling occurring. The samples could be easily cut with a razor blade and no boundaries, such as those found in the pressed disks, were apparent.

The ease with which the camphene sublimes results in a natural etching process. This etching very clearly shows any crystal boundaries that intersect the surfaces of the samples. The pressed disks always exhibited these boundaries, whereas the grown samples did not. Samples that were allowed to cool naturally in a test tube or petri dish also showed such boundaries.

For most globular molecules it is found that the phase stable immediately below the melting point is optically isotropic in conformity with the cubic structure exhibited by the plastic crystals in the first solid phase. Passing below the transition point, the crystal structure becomes anisotropic and the crystals are then birefringent.[11] At room temperature camphene exists in the body-centered cubic form. Therefore the crystals should be isotropic and should not rotate plane polarized light. This condition should exist whether or not the sample is a single crystal. However,

the presence of macroscopic crystal boundaries should be detectable, as these boundaries effectively present discontinuities in the medium at which reflection of light will occur.

An intense beam of light from a carbon arc was collimated by a simple positive lens and stopped to a diameter slightly less than that of the sample. The conical section of the crucible was removed as before, but the crystal was left in the Pyrex tube. The ends were carefully trimmed flat and kept as nearly parallel as possible. The sample was viewed against a black background with all other light excluded. The beam was passed through the samples parallel to the cylindrical axis when tests were made for reflections and internal scattering. The Tyndall effect, or internal scattering would be present if the single crystal contained foreign solid particles having different optical constants, i.e., refractive indices, from the main single crystal.

In the pressed disks, and also in samples allowed to cool naturally, the boundaries showed distinctly. The only reflections that were encountered in the grown samples occured at the end faces. There was also a conspicuous absence of internal scattering. It was noted that the insertion of a grown crystal in the beam did not appreciably affect the collimation, as observed on a screen placed a short distance from the end of the sample. The pressed samples, as a result of the multiple reflections, destroyed

the collimation.

CAMPHOR

Grown samples of d-camphor, as long as they were kept above the transition temperature, exhibited essentially the same optical characteristics as the dl-camphene crystals. Internal scattering was absent, and no crystal boundaries could be seen. The samples were transparent and of a waxy consistency, and they could be easily cut without crumbling. The samples could not be left exposed for any length of time at elevated temperatures, since they sublime readily.

CHAPTER VII

CONCLUSIONS

From the experiments conducted, it is fairly safe to conclude that single crystals of the three compounds can be grown by the methods discussed. Although the grown samples exhibited marked differences from polycrystalline samples, positive proof could most probably be obtained only through thorough x-ray analysis. This in itself would present definite problems, since the samples are much larger than those usually investigated using x-ray techniques, i.e., of the order of millimeters. Another problem would stem from the fact that these compounds are not effective scatterers of x-rays as a result of the internal rotation; and consequently, the patterns would probably not be sharply defined.[11]

The binding energy of molecular crystals arises from the average interaction of an original dipole moment, either permanent or a fluctuating dipole moment associated with the instantaneous electronic configuration, and the induced moment in the neighboring atoms.[13] These attractive electrostatic forces, van der Waals forces, are relatively weak (of the order of 3 Kcal/mol) and it is perhaps surprising that large single crystals of these substances can be grown. This is most probably the reason why such slow rates are

required to grow these crystals, as compared to rates resulting in single ionic crystals using the same methods. The binding energies of ionic crystals are approximately 100 times as great as those of molecular crystals and growth rates as high as five to six cm/hr, for much larger crystals, have been reported.[14]

Since camphene and camphor both sublime quite readily, one would expect that single crystals could be grown from the vapor. This would allow the formation of camphor crystals in the hexagonal phase, stable below the 97°C transition point. Camphene grown from the vapor would be of the same form as that grown from the melt.

ACKNOWLEDGMENTS

I wish to express my appreciation to Dr. John R. Green for presenting the problem and for his helpful suggestions; and to Mr. Carl Scheie for his contributions during the course of the investigation.

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