bombarded silicon with protons of energies between 200 keV to 1 MeV. They also observed diffusion enhancement and obtained diffusion lengths $L$ for the defects of 1.4 to 3.5 $\mu$m (at 900°C), depending upon dislocation density of the silicon. From the relatively high migration energy of the defects it is conjectured by these authors that mainly divacancies are observed. Further experiments are necessary to resolve the discrepancy of the different $L$ values. In particular, it is desirable to determine the defect migration energy and compare it to the values of Corbett and Watkins (single vacancy) and Baruch et al. (divacancy). Such experiments are planned.

**SUMMARY**

It has been shown that the bombardment of silicon with low-energy ions is a useful method to achieve high enhancement and obtained diffusion lengths $L$ for the defects of 1.4 to 3.5 $\mu$m (at 900°C), depending upon dislocation density of the silicon. From the relatively high migration energy of the defects it is conjectured by these authors that mainly divacancies are observed. Further experiments are necessary to resolve the discrepancy of the different $L$ values. In particular, it is desirable to determine the defect migration energy and compare it to the values of Corbett and Watkins (single vacancy) and Baruch et al. (divacancy). Such experiments are planned.

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**INTRODUCTION**

In most examples of crystal growth one finds that, after attaining stable size, a typical primary nucleus grows into a crystallite having a discrete crystallographic orientation. Generally speaking, this continues to develop as a single crystal until it impinges either upon external boundaries or upon other similar crystallites advancing from neighboring nuclei. Certain systems are known, however, in which primary nuclei are seemingly incapable of such development, each one giving rise instead to a more complicated structure of the kind shown in Fig. 1. This consists of a radiating array of crystalline fibers, all having the same fiber axis and possessing, therefore, the unusual property of branching in such a way that the crystallographic orientation of a branch departs slightly but appreciably from that of its parent fiber. In other words, it is a characteristic property of these particular systems that primary nuclei initiate the formation of polycrystalline aggregates which are more or less radially symmetric. The growth of these aggregates—which are known as spherulites—is both exceptional and (in terms of current theories of crystallization) anomalous, and satisfactory elucidation of the factors which give rise to and control spherulitic crystallization is a long standing problem in the theory of crystal growth.

Spherulites which occur naturally in silicate minerals found in igneous rock strata were studied extensively by...
Mineralogists toward the close of the last century.\textsuperscript{1,2} Somewhat later, artificial spherulites grown in organic \textsuperscript{3,4} and inorganic \textsuperscript{5} compounds received considerable attention from crystallographers in the early years of the present century. More recently, it has been discovered \textsuperscript{6,7} that all high polymers crystallize from the melt or from concentrated solution with a spherulitic habit; as a result, the problems presented by spherulitic crystallization are currently exciting renewed interest and also achieving some technological importance. Many attempts have been made over the years to resolve these problems. But, almost always, the fragmentary development of the subject and the preoccupation of workers of various periods with only one or two of the many known types of spherulite-forming system (which are tabulated presently) have conspired against a general and satisfactory solution. Bernauer,\textsuperscript{8} for example, studied spherulitic crystallization brought about in organic compounds by the addition of colloids, and attributed the phenomena he observed to crystalline disorder introduced by foreign particles becoming trapped in growing crystals. On the other hand, in discussing the growth of spherulites in high polymers, Bunn\textsuperscript{8} has emphasized the role of molecular entanglements which are considered to impede the rearrangement and alignment of molecular chains, thereby restricting the dimensions attainable by individual crystallites. Neither of these representative points of view is without substance in its own particular field of application, but both are obviously inappropriate as general explanations for spherulitic crystallization: it would clearly be unrealistic to ascribe spherulitic growth in organic compounds to molecular entanglements, or to suppose that spherulites in high polymers are attributable to the influence of foreign particles of colloidal dimensions.

For the most part, other discussions\textsuperscript{9-11} of spherulitic crystallization have dealt similarly with specific systems, and little attention has been paid to the problem of relating behavior in one system to that in another.

There is, nevertheless, a remarkable resemblance, both in manner of growth and in morphological detail, between spherulites grown in materials whose chemical structures vary widely and whose physical properties differ from one another quite drastically in most other respects. Many spherulites, for instance, share as a peculiarity of crystal habit the growth of twisted fibers.\textsuperscript{3,4,12,13} Indeed, the similarities between spherulitic crystallization in a wide range of substances—organic and inorganic, polymeric and nonpolymeric—are so pronounced that they can scarcely be coincidental. They suggest, rather, the agency of certain mechanisms of crystal growth which, although exceptional in the sense that they are effective only in spherulite-forming systems, are nevertheless common to all of these materials regardless of their otherwise unrelated properties.

Whatever these mechanisms may be, it is clear that they cannot be related too specifically to the molecular characteristics of any one or two species. It should be possible, therefore, to account for mechanisms of spherulitic crystallization on a unified basis, and in terms sufficiently general as to be applicable to spherulite-forming systems of all known types. From such a general standpoint, behavior in individual systems might then be interpreted in finer detail in terms of their specific properties.

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In the present paper we attempt to gain fresh insight into the causes of spherulitic crystallization, partly by re-examining earlier experimental findings and partly by considering new evidence drawn largely from recent studies of spherulitic crystallization in high polymers.

THE OCCURRENCE, GROWTH, AND PROPERTIES OF SPHERULITES

Occurrence

Among materials in which spherulitic crystallization has been observed, the better known examples are the following:

(A) Minerals crystallized from viscous magmas; and devitrified glasses in general.3
(B) High polymers crystallized from the melt.14
(C) Organic compounds crystallized from melts to which certain modifiers (generally “thickeners” which increase melt viscosity) have been added.4,15
(D) Inorganic salts crystallized by metathesis in gelatine.5
(E) Inorganic salts crystallized from solution in the presence of traces of surface active impurity.15
(F) Organic compounds which yield associated melts.16 (In essence, these may not be much different from C since the purity of most organic compounds usually leaves much to be desired.)
(G) Substances which, in certain ranges of temperature, exist as liquid crystals.16

These may be grouped into three categories: types A, B, and C in which spherulites grow from melts of relatively high viscosity; types D and E in which surface activity is probably important; and finally types F and G which call for special attention. In this paper we are concerned mainly with spherulitic crystallization from the melt in systems which fall in the first category, and the conclusions we are able to draw prove to have obvious implications with regard to the remaining categories.

Our principal concern, then, is with crystallization in liquids whose properties differ from those of simple liquids in two notable respects. Spherulite-forming melts not only have viscosities substantially higher than those of simple liquids—higher by at least two orders of magnitude—but, in addition, they crystallize much more slowly. For example, one generally finds in simple liquids that an approximate relation \( G = \mu \Delta T \) holds between \( G \), the velocity of advance of a growing crystal face, and \( \Delta T \), the supercooling, where \( \mu \) assumes values in the range 1–100 cm sec\(^{-1}\)C\(^{-1}\).17 In spherulite-forming melts, on the other hand, the dependence of \( G \) upon \( \Delta T \) is more complicated, but values of \( G/\Delta T \) are typically about 10\(^{-4}\) cm sec\(^{-1}\)C\(^{-1}\); seldom are they much larger than this and in some instances they fall as low as 10\(^{-5}\) cm sec\(^{-1}\)C\(^{-1}\). This slow crystallization, nevertheless, follows a course similar to that found in simple liquids, and takes place by three-dimensional nucleation and by crystal growth dependent, apparently, upon two-dimensional surface nucleation.18,19 The principal difference is that in spherulite-forming melts both rates of nucleation are small, seemingly because the diffusion processes by means of which molecules are able to present themselves with appropriate orientations at growth sites are severely impaired by unusually large melt viscosity. These melts, therefore, may be supercooled with ease, many of them to the extent of forming metastable glasses. Their isothermal crystallization is usually carried out at supercoolings of at least 5°C, and often as much as 100°C. In this respect, spherulites are generally grown under conditions quite different from most other crystals.

Modes of Growth

Under isothermal conditions, the growth of a spherulite from a supercooled melt follows a characteristic pattern regardless of the particular substance under study. Growing out from a primary nucleus as center, one finds a spherical (or cylindrical)30 body of the type shown previously in Fig. 1. Typically, such a spherulite consists of many crystalline fibers whose lateral dimensions are remarkably constant and which, through repeated branching, are uniformly space filling throughout the radiating aggregate. A study of extinction behavior under the polarizing microscope,20 or of microbeam x-ray diffraction,22 indicates that some preferred crystal axis always lies parallel, or almost parallel, to the radial direction. It is this result which tells us that the fibers branch in a manner which, unlike dendritic branching, is noncrystallographic. By this term we imply, first, that observed angles of branching are not simply related to the geometry of the crystal lattice and, secondly, that the crystallographic orientation of a parent fiber is not preserved in its daughter fibers. Indeed, one might describe spherulitic branching more appropriately as a splitting in which two distinct daughters emerge from the tip of a parent fiber at some arbitrary, but generally small, angle. In the following account, we refer to this process as “small-angle branching.”

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16 J. W. Tiller, “Principles of Solidification,” in *The Art and
In many spherulites grown in systems of types A and C, and also in some polymer spherulites which have grown at sufficiently small supercoolings for the radial fibrous arms to be coarse and well separated from one another, it may easily be seen by direct observation\textsuperscript{13,15,23} that discrete and relatively isolated fibers are the first product of crystallization. In other instances, including the majority of polymer spherulites, one finds more commonly that the fibers are very fine (fibrils) and so densely packed that the presence of uncrystallized melt between them cannot be detected by visual observation. It was inferred some years ago on the basis of indirect evidence, however, that even these spherulites consist initially of discrete fibrous crystals immersed in uncryatalized melt,\textsuperscript{13} a view which has since been substantiated by studies of light scattering\textsuperscript{24} and of bulk crystallization kinetics.\textsuperscript{25} Thus, for the systems under consideration, it may be stated with generality that, as first formed, spherulites consist of fibers or fibrils separated to a greater or lesser degree from one another by layers of as yet uncryatalized melt. This situation certainly obtains until after the radial growth of the spherulites is complete. Then, depending upon the nature of the system and upon prevailing experimental conditions, the layers of melt either remain uncryatalized indefinitely or they crystallize slowly to fill in the over-all structure. This further crystallization, which is to be identified with the process known to kineticists as secondary crystallization,\textsuperscript{25} is largely associated with slow lateral growth (coarsening) of existing fibers, but it may also be aided to some extent by the formation of new branches. In some instances secondary crystallization follows rapidly on the initial growth of fibers while in others it is sluggish. In polymers it is particularly slow and proceeds at steadily decreasing rates over long periods of time, apparently never quite reaching completion.

Early stages in the development of spherulitic aggregates are again very similar in most of these systems. As growth begins from nuclei, more or less parallel bundles of fibers are observed to fan out gradually like wheat sheaves,\textsuperscript{4,7} only to assume spherical (or cylindrical) shape at some finite, though frequently small, size. Radial growth then continues uniformly in all directions until the spherulites impinge one upon another and form polyhedral interspherulite boundaries. Growth from these sheaf-like precursors is characteristic both of polymeric and nonpolymeric systems and is often evidenced by “double-leaf”\textsuperscript{7} structures left behind near the centers of the spherulites.

However, there is some variability in behavior at these early stages of growth. In practice, many of the primary nuclei which initiate spherulitic growth are heterogeneous in nature, and consist presumably of disordered crystal layers absorbed on the surfaces of impurity specks. Spherulites may then grow from these nuclei without sheaf-like precursors being formed [see, for example, Fig. 8(a)]. Sears\textsuperscript{4} has suggested that, under certain circumstances, primary nuclei may be formed homogeneously by nonclassical means, and has based an interpretation of spherulitic crystallization upon this possibility. The preponderance of cases in which sheaf-like precursors are formed, however, is more consistent with the view that development into a spherulitic habit is, for the most part, a property of fibrous crystals which possess the ability to branch noncrystallographically.

**Properties of Spherulites**

In subsequent discussions, the terms (a) compact or open, (b) coarse or fine are used to describe the textures of spherulites, and it is convenient to define them at this point. At transient stages in crystallization, we have seen that spherulites consist of radiating arrays of fibers immersed in as yet uncryatalized melt. At any such stage, or at the termination of growth, the word compact is used to describe a situation in which a large proportion of the material within the boundary of a spherulite has already solidified. A more open structure, on the other hand, is one in which the fibers are separated to a relatively greater extent by uncryatalized melt. A coarse texture is one in which the fibers or fibrils—or, in some polymeric cases, composite fibrous arms (see later)—have relatively large cross sections; conversely, a fine texture denotes more tenuous radial fibrous units. Increases in coarseness frequently accompany increases in openness, though not in all instances.

The more significant properties of spherulites are the following:

1. Under isothermal conditions they grow at constant radial rate in almost all cases.\textsuperscript{14} Rare exceptions are found only under certain unusual circumstances\textsuperscript{28} and, for the moment, may be ignored. For present purposes we note, therefore, that at constant temperature spherulites generally grow in accordance with a linear growth law $G=dr/dt=f(T)$, where $r$ is the radius of the spherulite at time $t$ and $f(T)$ is a function only of the particular system under study and of the temperature. Experimental evidence leaves little doubt that this expression describes a steady-state process.

2. As temperatures of crystallization are increased the textures of spherulites generally become coarser, markedly so as the melting point is approached.\textsuperscript{14,28}

3. The morphology of the radial fibers (or fibrils) varies greatly from one system to another. Detailed information is limited in many cases but we may summarize as follows. Fibers in nonpolymeric spherulites are for the most part prismatic needles, more or less isometric in cross section and ranging from about $10^{-1}$ to less than $10^{-5}$ cm in “diameter.” Their fiber axes are commonly principal crystal axes. In polymer spherulites,

\textsuperscript{27} H. D. Keith and F. J. Padden, Jr., J. Polymer Sci. (1963) (to be published).
\textsuperscript{28} R. S. Stein and M. B. Rhodes, J. Appl. Phys. 31, 1873 (1960).
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on the other hand, the fibrils are commonly ribbon-like lamellar crystals ranging from about 100 to 1000 Å in thickness, from about $10^{-1}$ to 10 μ in width, and they are generally of considerable length. The long chain molecules are aligned normal to the planes of these lamellar fibrils, as a result of having folded back and forth fairly (though not completely) regularly on their edges during crystallization. Ribbon-like fibrils of this kind are found in the vast majority of crystallizable polymers. In other cases, finer fibrils of more rounded cross section are observed, often clumped together in composite structures of considerable complexity. Here again the molecules are aligned more or less perpendicularly to the fiber axes and these fibrils are probably chain-folded lamellae of much the same kind, except that for some reason their growth has been severely restricted in width.

So far, we have dealt only with substances of types A-C. From the standpoints of modes of growth and over-all morphology, however, spherulites in all of the systems A-G share the same general features. There are minor variations, of course, but the growth of discrete fibers which exhibit "small angle branching" is common to all of them.

Thus, we are led to the conclusion that spherulitic crystallization is a characteristic property of all systems in which two specific requirements are satisfied. First, conditions must be such as to favor the formation of crystals with a fibrous habit and, secondly, the fibers so formed must be capable of noncrystallographic "small-angle branching." When both conditions are met, geometrical considerations alone ensure the growth of polycrystalline aggregates with more or less radial symmetry. Individual fibers branch and develop into sheaves, sheaves continue to fan as further branching occurs and, inevitably, spherulitic growth must be the ultimate result. We have now to examine the means by which these requirements are fulfilled in the various systems under consideration.

**THE NATURE OF THE PROBLEM PRESENTED BY SPHERULITIC CRYSTALLIZATION**

Crystal growth, even from a nominally pure melt and under well-controlled conditions, is a complex and variable process, extremely sensitive to complications introduced by dislocations or traces of impurity. Simple and unqualified statements of general principle as to operative mechanisms can only be made, therefore, with due caution. Clearly, it would be impossible to account in elaborate detail for the course which crystallization follows at any one instant or in any one region of a spherulite during its growth. At best, we can only attempt to elucidate the significant physical factors which operate to induce spherulitic crystallization and, having done so, attribute them appropriately to the chemical structures and physical properties of the participating molecules.

It is beyond question, however, that the growth of a spherulite at constant radial rate represents a steady-state, and not an equilibrium, process. It is also clear from the large ratio of surface area to volume, and from the crystalline disorder associated with the many noncrystallographic branch points, that the spherulite does not represent an equilibrium crystal habit. Indeed, Morse and Donnay have reported that some inorganic spherulites are so unstable that they break up with almost explosive violence when disturbed mechanically. Now it is a matter of general experience that the only commonly occurring steady-state process by means of which crystals grow with a branching fibrous habit in simple liquids is dendritic crystallization. It is natural that one should seek to relate spherulitic crystallization to this process, but the following discussion makes it clear that this cannot be done satisfactorily in any simple way.

Dendritic crystallization is diffusion-controlled, and where it occurs in supercooled melts, has been explained in terms of the transport of heat across the solid-liquid interface and the diffusion of latent heat away from growth sites. Dendrites formed in crystallization from supersaturated solution are accounted for similarly in terms of the diffusion of solute and dendrites grown from the vapor phase are discussed in terms of the diffusion of matter to growth fronts. In each case, a crystal face in contact with supercooled melt, supersaturated solution, or supersaturated vapor is considered to be unstable with respect to the formation of projections, particularly at its corners or edges where the supercooling or supersaturation is greatest. The tips of these projections remain points of maximum supercooling or supersaturation and, therefore, continue to grow preferentially, becoming fine crystalline spikes (fibers) which branch from time-to-time as the result of a corresponding instability of their lateral surfaces. Under ideal conditions, such a dendrite is a single crystal. Its various arms usually grow along equivalent crystal axes, and any branching which occurs is crystallographic. To distinguish between various dendrites on the basis of growth mechanisms we shall speak of "thermal" dendrites in describing those whose growth is controlled primarily by the diffusion of heat, and of "saturation" dendrites in describing those whose growth is controlled primarily by the diffusion of fresh material to growth fronts. It must be borne in mind that diffusion processes of both types (of heat and of matter) may, and frequently do, play a part in the growth of any given dendrite. In terms of our usage, however, it is clear that a dendrite growing in a pure metal is a thermal dendrite whereas a snow crystal is a saturation dendrite.

In view of the large supercoolings involved, it might seem attractive to attribute fibrous crystallization in spherulite-forming melts to the growth of thermal dendrites.
Fibrillation Caused by Impurities

The possibility that impurities may play a vital role in promoting a fibrous habit in spherulitic crystallization seems to have first received serious consideration from Bernauer who, in his classic monograph of 1929, described experiments in which he induced spherulitic growth in about one hundred organic compounds by adding impurities to their melts. The impurities he employed were mainly resins which, by their complex nature, made interpretation of results difficult. Bernauer concluded that, as the temperature is lowered, impurities separate out in the melt as fine droplets which impede growing crystals and, by causing extensive disorder, break them up into fibers. His explanation is well adapted to cases where colloidal suspensions are involved; however, since most spherulite-forming melts are almost certainly homogeneous liquids, it can scarcely be one of general validity. In fairness to Bernauer, however, we should point out that the interpretation to be advanced in the next section might well be regarded as a revision of his, but extended considerably in the light of modern concepts of crystal growth.

There is no doubt that impurities are present in appreciable concentration in almost all spherulite-forming melts. Attention has already been drawn, for example, to organic compounds in which the property of growing spherulites is conferred upon one compound (the host) by the dissolution in its melt of small quantities—a few percent—of another (the impurity). Many such systems have been reported, well-known examples being those in which the host is resorcinol or malonamide and the impurity is tartaric acid or santonic acid. The dissolved impurity causes a disproportionately large increase in melt viscosity, and rates of primary and secondary nucleation are correspondingly reduced. At any given temperature, the radial growth rates of spherulites decrease substantially with increasing impurity content. A similar situation exists in most polymers. That these are also viscous and readily supercooled goes almost without saying; it is perhaps less obvious that they may also be said, with some justification, to be impure. A typical polymer melt is a multi-component system. It comprises molecules which vary widely in molecular weight, and there are often present in addition some molecules which, by virtue of stereo-irregular structure, crystallize less readily than their neighbors—or may even be totally incapable of crystallizing. Recent experiments have shown that low molecular-weight components and stereo-irregular components of the polymer are rejected preferentially by growing crystals, and they may be considered as impurities, therefore, for the purposes of the present discussion. It has been found, moreover, that polymer spherulites grow more slowly in the presence of higher concentrations of these impurities.

Once impurities are added to a melt, the rate of advance of a crystallization front no longer depends upon the diffusion of latent heat alone, but rather upon an interplay of the transport of heat and the diffusion of impurity. The growing crystal rejects impurity preferentially, and the concentration of impurity on the liquid side of the interface builds up to higher than its average value for the melt as a whole. For one-dimensional growth of a flat-ended crystal at velocity $G$ into an infinite melt, the concentration of impurity in the steady state is given by

$$C(x)=C_0 \exp\left(-Gx/D\right)+C_\infty,$$

where $C_\infty$ is the concentration of impurity at points remote from the interface, $C_0$ is the excess impurity concentration at the interface ($x=0$), and $D$ is the diffusion coefficient for impurity in the melt. This is plotted in Fig. 2. Unless the melt is stirred vigorously,
an impurity-rich layer of “thickness” \( \delta = D/G \) forms in the liquid at the interface. As we show presently, the existence of such a layer probably plays a large part in inducing a fibrous habit in spherulite-forming melts.

The influence of an impurity-rich layer surrounding a growing crystal depends greatly upon the properties of the system under study. For reasons which soon become apparent it is convenient here to contrast two particular types of behavior: (a) one-dimensional crystal growth in a column of molten metal such as represented in Fig. 2, and (b) radial growth of a sphere in a supercooled melt possessing those properties which are held in common by spherulite-forming melts of type B or type C. In both cases we discuss growth in the steady state only.

As regards the first of these examples, let us for the moment consider a pure metal. For this, the rate of crystallization, given by \( G = \mu \Delta T \), rises steeply with the value of \( \Delta T \) at the growth front and, in the steady state, is determined principally by the rate at which latent heat is transported away from the interface. If the temperature gradients on the two sides of the interface are small, \( G \) will be small, and conversely. When latent heat is carried away from the interface through solid and liquid phases [see Fig. 3(a)]—which presupposes that the melt was initially supercooled appreciably before crystal growth began—then it is clear that the advancing plane interface is unstable. Any projection on the surface resulting from some chance fluctuation reaches out into melt of increased supercooling and grows at an accelerated rate. The plane surface is, therefore, unstable with respect to the formation of thermal dendrites. However, when latent heat is carried away solely through the crystal [Fig. 3(b)] and the temperature rises as we move outward into the melt, a plane interface is obviously stable against perturbations of this kind.

The presence of an impurity-rich layer does not affect the instability materially in the first of these cases. We note that the temperature at the interface is very close to the equilibrium liquidus temperature of the most impure melt in the system—also at the interface. Since the equilibrium liquidus temperature rises as we pass outward through the impurity-rich layer (owing to decreasing impurity concentration), whereas the temperature decreases, the instability, if anything, is enhanced. In the second case [Fig. 3(b)] the effect of an impurity-rich layer depends upon the magnitude of the temperature gradient on the liquid side of the interface. In Fig. 3(c) we plot equilibrium liquidus temperature \( T_L(x) \), and ambient temperature \( T(x) \), through the impurity-rich layer for two possible values of the temperature gradient \( dT/dx \). When the steeper gradient applies, the liquid is nowhere supercooled in advance of the front since the difference \( T(x) - T_L(x) \) is positive and increases steadily. The plane profile of the growth front is then stable. With a less steep gradient, there may exist a region of melt in advance of the interface for which \( T(x) - T_L(x) \) is negative. The shaded area in Fig. 3(c), for example, corresponds to such a region which is

**Fig. 2.** Impurity concentration \( C(x) \) in advance of a growing crystal face.

\[ \text{(a)} \]

\[ \text{(b)} \]

\[ \text{(c)} \]

\[ \text{(d)} \]
then said to be "constitutionally supercooled." Under these conditions, small projections can form at the interface without additional latent heat having to be transported away; these projections, moreover, remain stable during subsequent growth. A plane profile is, therefore, unstable and, in the steady state, the system settles down in a cellular growth regime [Fig. 3(d)].

Only the more outstanding characteristics of this cellular crystallization are important here. The surface of the crystal becomes broken up into cells, commonly of hexagonal cross section (Fig. 4), which are separated by deep intercellular grooves. Experiments have shown that the impurity content of the solid phase is heavily concentrated at cell boundaries left behind in the wake of these surface grooves. It is fairly clear that relatively pure metal is deposited near the tips of the cellular caps, while rejected impurities diffuse laterally along the surface and collect in the grooves where the equilibrium liquidus temperature is depressed as a consequence. The existence of an appreciable temperature gradient in the crystal means that, as we proceed more deeply into the grooves, the temperature decreases and increasingly impure material is deposited on their walls. After some distance, which may be several cell diameters, the temperature is reduced sufficiently for solidification of the last remaining traces of impurity-concentrated melt. Cellular growth, brought about in this way by diffusional segregation of impurity, plays an important part in the generation of impurity substructures in metal crystals. Theoretical calculations of the average cell diameter $d$ have not been carried out in detail but it is clear from dimensional arguments that $d \approx \delta$. For metals $D = 10^{-5}$ cm$^2$ sec$^{-1}$, $G = 10^{-5}$ cm sec$^{-1}$ so that $\delta \approx 10^{-2}$ cm. In practice $d$ is found to depend also upon the value of $dT/dx$ at the interface, but falls in the range $5-10 \times 10^{-3}$ cm.$^{37}$

Cellular crystallization in metals, then, provides us with a well-documented example of how a plane crystal face responds to small perturbations of interface profile when instability is imposed by an impurity-rich layer. However, it cannot properly be regarded as giving rise to a fibrous crystal habit. It is true that elongated "fibrous" protrusions extend outward from the interface for distances some ten or more cell diameters, but these soon merge to form a single, though heavily disordered, crystal. Nevertheless, cellular crystallization gives us a valuable clue as to likely behavior in spherulite-forming melts, as we now show.

Let us now consider the hypothetical growth of a solid sphere within a spherulite-forming melt of type B or C. It is recalled that the properties of such a melt allow us to study relatively slow ($G \leq 10^{-3}$ cm sec$^{-1}$) crystallization at appreciable supercooling, and that a modest increase in impurity content—a few percent—reduces $G$ appreciably at any given temperature—often by an amount equivalent to a reduction in supercooling of at least several degrees Centigrade. We assume the radius of the sphere, like that of a spherulite, increases slowly but linearly with time, and we examine the stability of the spherical interface with respect to small fluctuations of profile. Latent heat must be carried away radially, but linear growth ($r \propto t$) at an appreciable supercooling can only mean that, in comparison with this transport process, growth is so slow as to require only a slight temperature gradient between the sphere and its surroundings. In other words, the ambient temperature throughout the sphere and its environment is maintained sufficiently uniform for us to regard the system as more or less isothermal, a view which is confirmed by comparing radial growth rates of spherulites and thermal diffusivities of the corresponding melts. Surrounding the expanding sphere there is an impurity-rich layer, and along an outward normal we may, therefore, plot impurity concentration $C(r)$, equilibrium liquidus temperature $T_L(r)$, ambient temperature $T(r)$, and local supercooling $\Delta T(r)$ as shown in Fig. 5. The thickness of this layer, again given by $\delta = D/G$, is now quite small—certainly less than $10^{-4}$ cm in most cases—

![Fig. 4. Cellular interface of a single crystal of zone-refined Pb containing 80-ppm Ag exposed by decantation of the melt. X333. (Courtesy of Dr. J. W. Rutter, General Electric Research Laboratory.)](image)

![Fig. 5. Impurity concentration $C(r)$, ambient temperature $T(r)$, equilibrium liquidus temperature $T_L(r)$, and supercooling $\Delta T(r)$ near the surface of a crystal growing into a spherulite-forming melt (schematic, arbitrary units for ordinates).](image)

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since $D$ is reduced by several orders of magnitude as evidenced by high melt viscosity. The gradient $d(\Delta T)/dr$ in the impurity-rich layer is accordingly quite steep, and renders the surface of the growing sphere extremely unstable since any small projection formed on it reaches out into regions of substantially greater supercooling.

It may be noted that any slight temperature gradient $dT/dr$ which might exist at the interface must be so directed as to further the instability, though its influence is heavily outweighed by that of the gradient $d(\Delta T)/dr$. Such a temperature gradient $(dT/dr)$ would be unable to promote the growth of thermal dendrites, however, principally because the value of $G/\Delta T$ in such a system is very small.

One might expect the instability of the surface to give rise to a cellular interface much as we have described previously. But, and this is one of the vital differences between systems which form spherulites and those which do not, cellulation now advances to an extreme and exaggerated degree as depicted in Fig. 6 where, for the present, curvature of the spherical surface and resulting divergence of the cells are both neglected. Whereas fairly rapid crystallization within the grooves on the cellular surface of a growing metal crystal is made possible by a temperature gradient with the crystal, there is no corresponding effect in the present case. The grooves contain melt of relatively high impurity content as before, but are now at ostensibly the same temperature throughout. Because of this, and because nucleation rates decrease markedly with increasing impurity concentration in these particular systems, lateral growth of the cells into the grooves is extremely, and increasingly slow. The properties of spherulite-forming melts, in other words, are such that the surface of a growing sphere is obliged to develop long fibrous projections separated one from another by uncrytsallized melt. Similar reasoning may be applied to show that in spherulite-forming melts the surfaces of a growing circular disk, or the faces of a growing polyhedral crystal, must likewise be caused to develop fibrous projections.

In order to see what the likely diameters of these fibrous projections are, we must consider the initial instability of a smooth interface. In Fig. 7, let us consider a small area of interface (assumed flat) with an impurity-rich layer extending a distance $\delta$ in the direction of growth (parallel to the $y$ axis). If a small projection of height $y'$ is formed on the surface, impurity diffuses laterally away from it and hinders the formation of neighboring projections within a certain "circle of influence." The radius of this circle depends upon a competition which takes place between growth and diffusion during the interval $dt$ in which the interface as a whole advances by the distance $y'$. In this interval impurity can diffuse parallel to the surface for a distance $\rho$ given approximately by $\rho^2 = Ddt$, and combining this with the relation $y' = Gdt$ we have $\rho^2 = Dy'/G = \delta y'$. In choosing an appropriate value for $y'$ we are guided by the following considerations. If $y'$ is much smaller than $\delta$, the diffusion of impurity from the projection is not distinguishable in effect from fluctuations in impurity concentration arising by other means. On the other hand, one must expect neighboring projections which are competing with the particular projection under consideration to interact with it before $y'$ reaches the value $\delta$. Probably we would not be far wrong if we compromise between these limits and take $y' = \delta/4$. Then we have $\rho = \delta/2$, and thus the diameters of the resulting fibers would be roughly equal to $\delta$.

Without a more rigorous investigation, which would be difficult to perform with realistic approximations, we must use caution and regard $\delta$ as determining the diameters of the fibers in order of magnitude only. However, one point is immediately obvious: the large viscosities and correspondingly low values of $D$ in spherulite-forming melts bring values of $\delta$ below $10^{-3}$ cm as an upper limit, and generally into the micron and submicron range. The fibers and fibrils found in spherulites have dimensions which do indeed fall in this range, and in forthcoming publications it will be shown that variations in coarseness of texture brought about either by changes in composition or by changes in temperature of crystallization correlate extremely well with corresponding changes in $\delta$. We believe, therefore, that the growth of fibrous crystals in spherulite-forming melts is attributable to cellulation and fibrillation on a fine scale, and brought about by a diffusional segregation of impurities in the manner we have described. We have yet to show how fibrillation caused by impurities leads to noncrystallographic branching, and consequently to results differing drastically from those found in metals, but, before passing on to this in the next section, let us pause for a moment to reconsider the commonly stated assertion that fibrous growth in spherulites is nucleation, and not diffusion, controlled.

In order that a diffusional segregation of impurity such as we have described can cause fibrillation at the surface of a sphere growing at constant rate ($r \propto \delta$), the value of $D$ must be sufficiently small to ensure that the
impurity concentration in the melt remains constant (at its initial value) except within small distances of the interface. The diffusion of impurity would otherwise outstrip slowly advancing growth fronts, and an extended radial concentration gradient would be set up, causing diffusion-controlled growth for which, in the steady state, $r \propto t$. That which we describe is, of course, diffusion-controlled growth or, more accurately, growth controlled by surface nucleation whose rate is severely modified from point-to-point by diffusion in the melt. The significant point, however, is that because growth rates are large relative to diffusional mobility, segregating impurities diffuse along the interface and over small distances only. There is no concentration gradient at points further from the center of the sphere than about $(r + \delta)$, and linear kinetics are observed, therefore, in the steady state. Nevertheless, there is a continuous tendency for equilibration between the impurity-rich layer and the bulk of the melt. Consequently, one would expect impurity species possessing relatively large diffusional mobility to be carried away radially from the interface, causing growth to become diffusion controlled in the conventional sense of the term. This prediction has in fact been confirmed experimentally in high polymers to which diluents of relatively low molecular weight have been added as impurity: isothermal spherulitic growth then departs from the linear $(r \propto t)$ law and approximates a parabolic $(r \propto t^2)$ law.

**SMALL-ANGLE BRANCHING**

Having shown that a crystal of spherical, or any compact polyhedral, shape growing in a spherulite-forming melt probably fibrillates once it is appreciably larger than $\delta$ in size, let us now inquire into the origin of small-angle branching. Singularities of many kinds, such as screw dislocations or local temperature gradients, can be envisaged which might cause fibers to branch, but there is no apparent reason why these should give rise to branching which is unmistakably noncrystallographic. The latter can only arise through the agency of misaligned surface nuclei, and we suggest that it comes about in the following way.

Invariably, any real crystal is disordered to some extent, not only in its interior but also at its surfaces. For our purpose, however, the precise nature of the surface disorder is not overly important, provided that slight deviations in crystallographic orientation are involved. It is of greater significance that the disordered regions are generally small, and presumably it is at these minute singularities that noncrystallographic branches are initiated. Nevertheless, we would expect singularities of this kind to be common to most growing crystals, and what we must explain is the observation that it is only in spherulite-forming melts that they act as effective nuclei for noncrystallographic branching.

Now it is a fundamental property of cellular crystallization in an impure melt that any perturbation of surface profile on a growing crystal is stable and persistent only if its size is commensurate with $\delta$. If much larger than $\delta$, it breaks up into a number of smaller cells; if much smaller, it is swallowed up by other topographical features of more propitious size. Singularities of
the type we are considering, therefore, have an opportunity to act as sources of persistent new growths only if $\delta$ is very small. This at once restricts us to impure melts having high viscosities. In such a melt we expect to find that as $\delta$ is decreased from a relatively large value (by some controlled variation of crystallization conditions) there is at first little likelihood of noncrystalllographic branches being formed. Surface disorder is present, but it is engulfed within the coarse fibers which are obliged to grow under these circumstances. As $\delta$ decreases, however, there is an increasing probability that one of the larger singularities at the shoulder of a growing fiber is of sufficient size that, with further growth, it becomes a persistent surface feature. If this new growth has a crystalllographic orientation which departs slightly from that of the parent fiber, it gives rise ultimately to a new fiber which diverges from the original. Thus, one initial fiber has split, in effect, into two fibers, each about $\delta$ in width and each growing along the same preferred crystal axis but misaligned slightly with respect to the other. As $\delta$ decreases further, the probability of such an occurrence increases correspondingly and, when $\delta$ is very small, almost any island of surface disorder, of whatever origin, becomes a possible source of noncrystalllographic branching. As far as branching is concerned, then, the essential difference between crystallization in simple liquids and in spherulite-forming melts is in the magnitude of $\delta$. Only in the latter do we have sufficiently small diffusion coefficients to ensure values of $\delta$ which are small enough for branching to be predominantly noncrystalllographic. Dendrites growing in melts of lower viscosity are subject to substantially larger values of $\delta$ and, for the most part, they branch crystallographically. Necessarily, such branching involves appreciable angles and, even if crystallographic branches were to form in spherulites, they generally would not develop to an observable extent because of impingement with neighboring fibers.

We infer from these considerations that frequency of noncrystalllographic branching varies inversely with the magnitude of $\delta$. This prediction is amenable to experimental test. In Fig. 8 we show three stages in the growth of a spherulitic aggregate in a thin film of malonamide containing 10% of d-tartaric acid as impurity. After crystallizing for some time at $80^\circ$C [Fig. 8(a)] the sample was cooled abruptly to $0^\circ$C. Further crystallization was slower and led to the development of fine overgrowths on existing fibers [Fig. 8(b)]. After a further period, these overgrowths developed into the structures shown under higher magnification in Fig. 8(c). We note that the fibers in Fig. 8(a), which are about $10^{-3}$ cm in diameter, did not branch during growth. On cooling to $0^\circ$C, however, $\delta$ is reduced and subsequent crystallization is with a much finer texture; most important, however, is the fact that radiating spherulitic growth began at the tips of the original fibers [Fig. 8(c)]. Portions of extinction crosses can be seen at these semicircular overgrowths, showing not only that the crystallographic orientation has radial symmetry, but also that the fine fibers are now capable of copious small-angle branching.

Similarly, in the case of spherulites grown in polymers, we have found consistently that coarser fibrils-formed under conditions where $\delta$ is relatively large—branch to a limited extent only, a circumstance which gives rise to the spherulites of very open texture commonly found at low supercoolings (see Fig. 9). When crystallized at higher supercoolings, however, these same polymers form spherulites with much finer textures—corresponding to smaller values of $\delta$—and these are observed to have very compact structures such as can be formed only in the presence of profuse small-angle branching. We have also found it to be a general result in spherulitic crystallization that the sizes at which sheaf-like precursors finally achieve spherical outlines decrease as their textures become finer, a further clear indication that small-angle branching becomes more frequent when $\delta$ takes smaller values.

We can only guess at the probable origins of the disorder responsible for this branching, and they are likely to be quite different in different systems. In the case of polymers, it is particularly easy to see how disordered layers of molecules could be deposited at growth fronts. In view of the fact that, in the course of crystallizing, molecular chains of considerable length are being extracted from a viscous melt and caused to fold on themselves many times, there is every reason to expect that maladjusted layers are laid down from time-to-time. In those particular systems in which the fibrils consist of chain-folded, ribbon-like lamellae, other mechanisms of branching are also possible. One such possibility is that a given lamella may develop a screw dislocation lying normal to its plane and thus be split into two parts which, on growing further, overlap. Because they are fine and lacking in rigidity, these overlapping lamellae may diverge from one another eventually. Such a mechanism, however, although likely to contribute to
branching in some polymer spherulites, almost certainly is not one of general applicability. In nonpolymeric spherulites, on the other hand, interpretations are clouded by our inadequate knowledge of the degree of perfection of the crystalline fibers. If these fine fibers possess mosaic substructures in the manner that larger crystals do, then the larger mosaic blocks exposed at growth surfaces—which would probably be about $10^{-8}$ cm on a side—would provide fertile sources for branches whose orientations deviate slightly from their parents. However, the fact that the fibers often twist in a manner suggesting the presence of axial screw dislocations indicates that this interpretation may merit less emphasis than we have previously placed upon it. More weight should perhaps be given to the disorder—much of it probably of a transitory nature—to be expected at the surface of a growing crystal which is bathed in melt containing a relatively high concentration of crystallization-rejected impurities. We might well expect the formation of misoriented surface nuclei or of small islands of impurity-rich precipitate under these conditions. Further experiments are required to clarify these details, but we believe the essential result to be beyond doubt: that is, any singularity in the form of a small misoriented region on the surface of a fiber is a potential source of noncrystallographic branching, provided that its size is commensurate with the value of $\delta$ for the system in question.

Once a radiating growth pattern is established as a result of small angle branching, fibers diverge one from another and might be expected to coarsen. In fact, they do not do so to any extent since, on one hand, their widths are governed by $\delta$ and, on the other hand, further branching intervenes. In many cases, there are probably more potential branching possibilities than can be used effectively so that only those embryonic branches persist which find room to grow among their neighbors. But when $\delta$ is relatively large, either because the supercooling is small or because the melt viscosity is not excessive, there are fewer branching possibilities and these depend more specifically upon the particular type of disorder which is responsible. Thus, it is not surprising that spherulites of coarse texture have open structures and often present irregular outlines. Nor is it surprising to find that the limited branching observed in these cases commonly involves larger, though still noncrystallographic, angles (see Fig. 9).

THE OVER-ALL PROCESS OF SPHERULITIC CRYSTALLIZATION

We may now draw upon the principal conclusions of earlier sections and combine them as follows. A crystal growing in a mixed melt of type B or C becomes unstable with respect to an exaggerated type of cellulation (fibrillation) once its size exceeds $\delta$ appreciably, and a fibrous habit is established as a result. Relatively high melt viscosity plays a major part in bringing this about. It so reduces rates of crystal growth, and so reduces the widths of impurity-rich layers at growth fronts that, in comparison with local variations in impurity concentration and in supercooling, temperature gradients have little influence. It also has the further, and vital, significance that it causes $\delta$ to be small, and generally small enough that fibers branch noncrystallographically. Then, regardless of the nature of the primary nucleus that initiates crystallization, bundles of fibers are formed which tend to fan into sheaves. Ultimately, a more or less spherical aggregate consisting of radial fibers must develop, each fiber having much the same fiber axis as every other. Unlike the case of cellulation in a metal crystal, the final result cannot be a single crystal, but must be a spherulite.

Within the broader field of crystal growth in general, a spherulite might well be regarded as a particular type of saturation dendrite which, in crystallizing from the melt, abstracts relatively pure material from the liquid and rejects impurities. Its growth is diffusion-controlled in the very real sense that its fibrous habit is certainly dictated by diffusion processes, but the kinetics of growth nevertheless bear little direct evidence of this. The melt is extremely viscous so that, although fibers grow fairly slowly, they nevertheless do so at a rate which is fast in comparison with the rate at which impurities can diffuse away. Rejected impurities are then trapped between the fibers and, as a consequence, there are no concentration gradients outside the confines of the spherulite. As a result, the kinetics of radial growth are linear and seemingly indicative of growth processes controlled by nucleation, rather than diffusion.

In the final section of the paper we review briefly the implications of this interpretation with regard to spherulite-forming systems of the many various kinds we have listed earlier.

SPHERULITIC CRYSTALLIZATION IN VARIOUS SYSTEMS

Type A : Mineral Spherulites

Although the morphology of mineral spherulites has been studied widely, direct evidence is lacking as to their mode of growth. The magmas from which igneous rocks are formed have high viscosities, and fractional crystallization is known to play a large part in their solidification. Fine fibrillation due to impurities is a likely consequence, and there is every reason to believe that spherulitic growth follows a course similar to that we have described earlier for systems of types B and C.

Types B and C: High Polymers and Impure Organic Melts

Much of what has been said earlier is based upon a knowledge of behavior in these systems, and this need not be elaborated further. However, we may note in passing that, in view of the diversity of synthetic high polymers which are available for study—covering wide ranges of molecular weight and stereoregularity—these materials are particularly suitable for putting to experimental test the various predictions we have made. Extensive studies have already been carried out and are being reported more fully elsewhere; here we merely summarize the principal results. Coarseness of texture follows variations in $\delta$ as anticipated and, insofar as available data allow the comparison to be made, the magnitude of $\delta$ agrees quantitatively with the dimensions of fibrils within experimental uncertainties (one or perhaps two orders of magnitude). Dependence of small-angle branching upon fineness of texture, and the onset of nonlinear radial growth when mobile impurities of low molecular weight are used, have also been confirmed as predicted.

Types D and E: Modified Solution Growth

Clearly these are cases where a different crystallization mechanism must be operative but, in terms of what has already been said, we may not have far to go for an understanding of its nature. All that is required for spherulitic crystallization is the establishment of a fibrous regime in which the fibers branch noncrystallographically. In systems of type D, where ionic salts are crystallized in a gelatinous medium, it is likely that a tenacious adsorption of gelatine (a polyelectrolyte) on all but the most rapidly growing crystal faces—the tips of fibers—greatly impedes nucleation processes. The importance of high viscosity in these systems, to which attention was drawn by Morse and Donnay, may well derive from the fact that it prevents fast transport to growth fronts so that the lateral surfaces of fibers grow slowly enough to become extensively poisoned by adsorbed gelatine. Typical systems of type E are aqueous solutions of salts such as potassium perchlorate to which the addition of as little as one part in $10^4$ of certain dyes is known to cause drastic habit modification and promote spherulitic growth. These dyes are known to be strongly adsorbed on the surfaces of the crystals and appear to act in much the same way as gelatine. Noncrystallographic branching in systems of both types D and E presumably has its origin in misoriented overgrowths brought about, in the main, by interference from strongly adsorbed impurity.

Types F and G: Associated Melts and Liquid Crystals

These systems, which we consider last, are the least studied and certainly the least well understood. As fluids, it is clear that they possess unusual properties, particularly those of type G, and these suggest the formation of relatively stable complexes which resist being broken down or otherwise modified as a preliminary to crystallization. Complexes of this kind might in a sense act as transient “impurities” and cause fibrillation in a manner similar to that we have discussed previously. Their average lifetime need not be long: provided the fibrillation is accompanied by small-angle branching, spherulitic growth would presumably follow.

CONCLUSIONS

The rationale we have presented is consistent with established principles of crystal growth and is capable of explaining semiquantitatively, and on a unified basis, the principal observed facts of spherulitic crystallization, both in polymeric and in nonpolymeric systems. It has the generality and flexibility needed to account for superficially similar behavior in this wide range of materials, without invoking to an unreasonable degree specific characteristics of particular molecular species. A prominent result is the prediction that the quantity $\delta$ is a size-determining parameter controlling both the coarseness of crystalline texture and the frequency with which fibers branch. A series of papers is in preparation which provide experimental confirmation of this, and of other predictions which have been made.