Eutectic Solidification in the NaF-MgF$_2$ System

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The compound NaMgF$_3$ occurs in the system NaF-MgF$_2$ and forms a eutectic with either component. The eutectic between NaF and NaMgF$_3$ has been unidirectionally solidified and the phase morphology and crystallography examined by optical and electron microscopy coupled with electron diffraction. Solidification with the "complex-regular" morphology from faceted cellular projections on the solid/liquid interface occurs for compositions on both sides of the eutectic point. Extensive regions of rod-like morphology occur in specimens where one of the macrofacet planes, constituting the faceted projections, is perpendicular to the direction of heat extraction.

An analysis of twinning observed in the NaMgF$_3$ phase shows that it occurs in accommodation of lattice strain associated with a distortion of the unit cell axes on cooling from the growth temperature. These small distortions involve a progressive reduction in crystal symmetry from a cubic high temperature form to orthorhombic at ambient temperatures. The twins are not associated with the eutectic growth process in providing re-entrant edges to facilitate coupled growth of the two phases.

1. Introduction

In recent years there has been widespread interest in eutectic solidification. Although most attention has been given to "metal" and "organic analogue" systems [1], a limited number of studies of binary alkali halide systems have been reported [2-4]. A systematic investigation of a series of mixed fluoride eutectics has recently been undertaken in this laboratory. Of particular interest were the LiF-MgF$_2$ and NaF-MgF$_2$ systems. A description of the former has been given elsewhere [5]. In this paper the mode of solidification for a eutectic in the NaF-MgF$_2$ system is discussed.

The relevant phase diagram [6], indicates the formation of two eutectics. The lower melting point eutectic, between NaF and NaMgF$_3$,occurs at 77 mol % NaF and 820°C, and the second eutectic, melting at 1000°C occurs at 40% NaF between NaMgF$_3$ and MgF. However, a previous cursory study of this system [7] indicated the formation of a eutectic with constituent phases NaF and MgF$_2$.

In the present work, solidification of a range of NaF-MgF$_2$ mixtures has confirmed the presence of two eutectics, in agreement with the phase diagram [6]. This paper is concerned with the eutectic in which the constituent phases are NaF and NaMgF$_3$.

2. Experimental

Details of the directional freezing technique employed in this study have already been given [5]; it is sufficient to mention here that alloys prepared from carefully weighed proportions were melted in air in graphite crucibles and were subsequently directionally solidified by downward withdrawal of the specimen. Phase identification was accomplished by the Debye-Scherrer X-ray method. Polished sections and fracture surfaces of the resultant two-phase structure were examined by optical microscopy and by scanning electron microscopy. Preferential chemical dissolution of one of the eutectic phases provided single phase fragments for transmission electron microscopy. Both these fragments and thin two-phase cleavage slices were attached to adhesive electron microscope grids and examined in a JEM.200 electron microscope in both diffraction and imaging modes of operation. Operation of this instrument at 200 kV reduced specimen degradation, on ex-

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posure of the fragment to the electron beam, to a level which facilitated the recording of good quality transmission images and corresponding selected area diffraction patterns.

3. Observations of Microstructure and Crystallography

3.1. Phase Morphology

Examination of polished sections, etched in 50 % methanol-water, revealed that this eutectic solidified with a "complex-regular" morphology. The microstructure consisted of an array of "triaxial growth units", each of which was composed of parallel alternate lamellae of the two phases which extended on either side of, and in a direction perpendicular to, three interconnected "spines". The spines intersected along a line whose direction was parallel to the axis of heat flow. Quench experiments performed during the solidification of several specimens revealed that the solid-liquid interface is comprised of an array of orthogonal macrofacets. A direct correspondence between projections on the interface and "triaxial growth units" was established and it is envisaged that the complex-regular morphology develops when these faceted cellular projections advance into the melt as solidification proceeds. The connecting "spines" grow ahead of the lamellar side branches and the point at which the line of intersection of the three "spines" meets the quenched interface projects furthest into the melt.

The arrangement in which the macrofacet planes, which constitute the solid-liquid interface, are equally inclined to the growth axis, was that most frequently observed in directionally frozen ingots of this alloy. A transverse section through a grain which typifies this case is depicted in fig. 1a. In this micrograph the connecting "spines" of the light etching phase, shown by X-ray and electron diffraction to be $NaMgF_3$, make angles of 120° with each other. Although the microstructure adjacent to these spines is lamellar, the plates of $NaMgF_3$ oscillate in thickness, after extending a short distance, and ultimately impinge on one another, enveloping the NaF phase and resulting in a rod morphology. The complex nature of the transition is exemplified in fig. 1b. The corrugations on the lamellae, which mark the onset of this transition, extend in the direction of plate growth, interrupted occasionally by mechanical or thermal fluctuations which produce banding, delineating successive positions of the solid-liquid interface. One

such corrugated plate, detached from the microstructure by the dissolution-fragmentation technique, is shown in fig. 1c. On this micrograph the trace of the plane of transverse section (figs. 1a and b) is indicated by the continuous line and the traces of intersection with the local solid-liquid interface by the broken line.

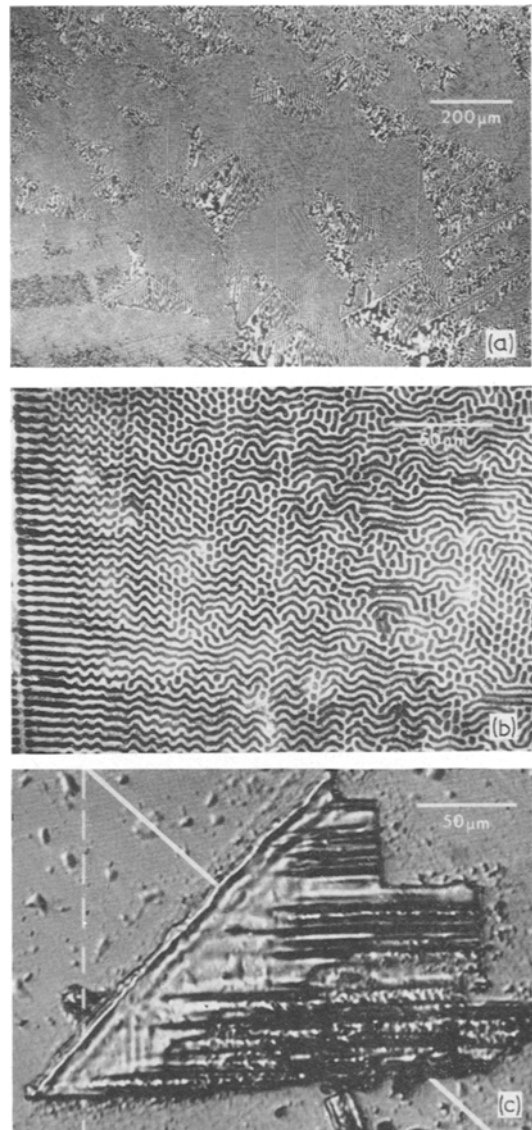A second configuration which was occasionally observed results when one of the three macro-

Figure 1 (a) Transverse section of the "complex-regular" eutectic grain. (b) Transverse section illustrating the lamellar to rod transition away from the spine in a "complex-regular" unit. (c) A corrugated lamellar plate extracted from the two phase structure.

facet types on the terraced interface is oriented such that its plane normal is parallel to the externally imposed growth direction. It is envisaged that this results in the development of extensive regions with a rod-like morphology. Longitudinal and transverse sections from a typical region are shown in fig. 2. Occasionally intermediate orientations of the "triaxial units" were observed in smaller outgrowing grains.

Complex-regular structures were produced in both "hypo" and "hyper"-eutectic melts for all growth rates in the range 5 to 80 mm/h. In all specimens a predominance was observed for large grains where the "triaxial units" were oriented such that all macrofacets on the terraced solid-liquid growth front were approximately equally inclined to the specimen axis.

3.2. The Triaxial Growth Unit

The morphology within a grain of complex-regular eutectic consists of an array of "triaxial growth units" in parallel orientation. Using information gained from optical and scanning electron microscope examination of quenched interfaces, polished sections and cleavage frag-
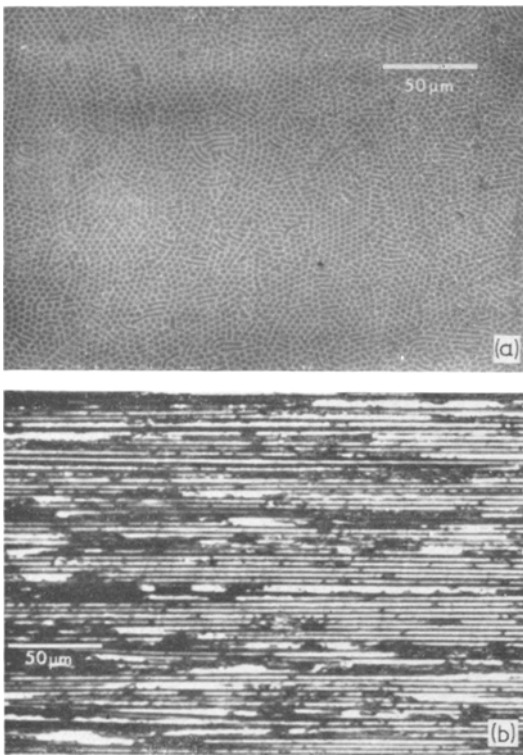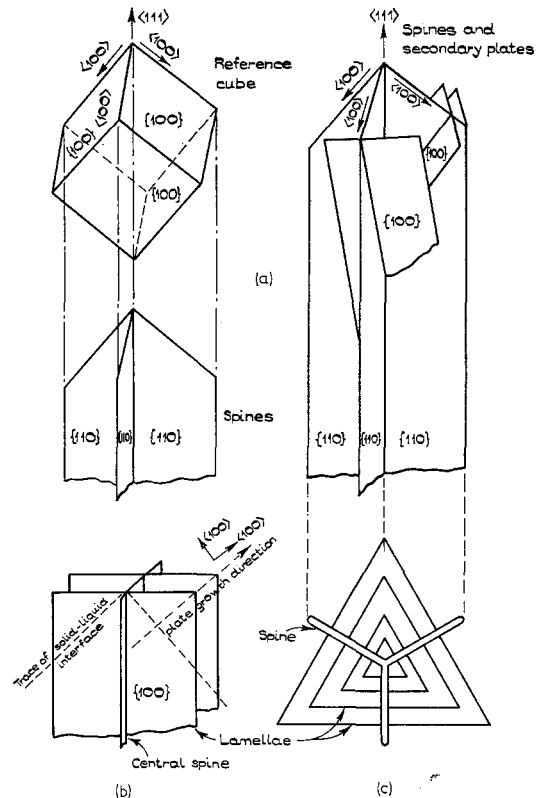
Figure 3 (a) An illustration of the interconnected form of the "faceted" phase in relation to a reference cube. (b) The lamellar side-plate configuration. (c) Transverse section through an idealised "complex-regular" unit.

ments, and neglecting the breakdown of the lamellar morphology into rods, it has been possible to construct a simplified model of the NaMgF$_3$ phase morphology in relation to a unit cube (which later is shown to be equivalent to the crystallographic unit cell for a high temperature modification of NaMgF$_3$). A sequence of sketches depicting the development of the structure is reproduced in fig. 3. The pyramidal projections resemble sections of a cube so oriented that the {100} cube planes are parallel to the macrofacets on the solid-liquid interface. The "spines" extend as {110} planes along ⟨100⟩ directions following the cube edges, and the line of intersection of the three spines lies along a ⟨111⟩ cube direction such that the apex of the projection corresponds to a cube corner. The lamellar side plates extend from the spines parallel to {100} planes.

3.3 Crystallography of the NaMgF$_3$ Phase

It is believed that the growth characteristics of

Figure 2 (a) Transverse and (b) longitudinal sections through a eutectic grain with a rod morphology.

the "faceted" phase are dominant in the development of the "complex-regular" eutectic morphology [1, 8]. It is, therefore, important to identify the facet planes and growth directions for NaMgF$_3$ which is believed to possess "faceted" growth characteristics.

Chao et al [9] have shown that NaMgF$_3$, both in its natural form as the mineral "Neighborite" and as prepared by reaction of NaF and MgF$_2$, is isostructural with perovskite (CaTiO$_3$). At ambient temperatures the unit cell is ortho-rhombic of dimensions $a = 5.363$ Å, $b = 7.67$ Å, $c = 5.503$ Å. However, on heating to 950°C structural changes occur which result in different rates of expansion of the lattice vectors. At 760°C a and c become identical and the unit cell adopts a tetragonal symmetry modification with lattice basis vectors $a_t = 3.942$; $c_t = 3.933$. A further transformation occurs at 900°C when the unit cell becomes cubic.

Two reference systems are used in this work, an orthorhombic set of basis vectors, **a**, **b**, **c** and a cubic set **a'**, **b'**, **c'**. Directions and planes in the former system are designated subscript $_o$ and in the latter system subscript $_c$. The relationship between the lattice vectors of the orthorhombic and cubic structures is contained in the description:

$$\mathbf{a'} = \tfrac{1}{2}(\mathbf{a} + \mathbf{c})$$
$$\mathbf{b'} = \tfrac{1}{2}\mathbf{b}$$
$$\mathbf{c'} = (\mathbf{c} - \mathbf{a})$$

It is impossible to retain either the cubic or tetragonal modifications by quenching to room temperature. Transmission electron microscopy must therefore be performed on material which has transformed to the orthorhombic state.

Low index reciprocal lattice sections pertinent to the interpretation of prominent electron diffraction patterns were constructed from X-ray data reported by Chao et al [9]. The high temperature cubic structure would give rise to identical fourfold symmetric diffraction patterns for [100]$_c$, [010]$_c$ and [001]$_c$ incident electron beam directions. Extra allowed reflections arising from displacement of the ions in the cubic perovskite structure are present in electron diffraction patterns recorded from material which has transformed to the lowest symmetry state. These extra reflections, superimposed on the basic cubic pattern, render diffraction patterns recorded with the incident beam parallel to the [010]$_o$ (equivalent to [010]$_c$) and [10$\bar{1}$]$_o$ and [101]$_o$ (equivalent to [100]$_c$ and [001]$_c$

directions) easily distinguishable. These patterns, which are important in the interpretation of twinning modes discussed in the following sections, are reproduced in fig. 4.

Members of the perovskite family are frequently twinned as a result of cooling polycrystalline samples through the transition temperature. If the transformation of NaMgF$_3$ were to occur homogeneously, then long range lattice strain would accompany the anisotropic contraction of this phase. When the lamellae are sandwiched between plates of NaF a large strain energy may be avoided by the presence of a suitable configuration of "accommodation twins". The relative shrinkage of the b' and a' or c' axes which accompanies the cubic-tetragonal transformation may be accommodated by twinning across either (110)$_c$ or (011)$_c$ twin-composition planes. Twinning in this mode is referred to as "tetragonal" twinning. The contraction of c relative to a which occurs below 760°C may be accommodated by twinning across (100)$_c$ or (001)$_c$ composition planes. Since eutectic solidification occurs at 820 ± 10°C, which is below the temperature at which the tetragonal distortion begins, it was anticipated that only orthorhombic accommodation twinning would be present in lamellar plates of the NaMgF$_3$ phase.

3.4. Electron Microscopy and Diffraction

Plates of NaMgF$_3$ extracted from unidirectionally solidified regions of the eutectic were too thick to permit significant penetration of the 200 kV electron beam except in regions adjacent to the specimen edge. Surprisingly, diffraction patterns recorded from plates oriented for normal incidence of the electron beam revealed that without exception the lamellar interface plane was an (010)$_o$ plane. (101)$_o$, (10$\bar{1}$)$_o$ and (010)$_o$ interface planes should have occurred with equal frequency if the NaMgF$_3$ phase comprising each triaxial unit was a continuous single crystal. In addition, translation of the electron beam along the edge of the platelet by which it had been attached to the spine suggested that an orientation change occurred in this region. However, in the absence of corresponding transmission images these experiments were inconclusive. Optical examination of specimens which had been quenched to arrest the progress of unidirectional solidification, revealed that the microstructure adjacent to the position of the quench was similar to that for the directionally

solidified alloy, but on a finer scale. Plates extracted from this region were sufficiently thin to yield both selected area diffraction patterns and good quality transmission images (fig. 4).

Examination of plates by selected area electron diffraction confirmed that all plates had $[010]_O$ plane normals (fig. 4). The plates contained large numbers of fine parallel bands, image contrast for which was extremely sensitive to specimen tilting. This procedure produces systematic contrast reversal for adjacent bands and is characteristic of twin-boundaries across which small orientation differences exist. The trace of the interface plane between the crystal parts lies in $[101]_O$ or $[10\bar{1}]_O$ directions. Furthermore the interface plane was established to lie perpendicular to the plane of the plate from images recorded at various angles of specimen tilt. The twin-composition plane is either $(10\bar{1})_O$ or $(101)_O$, corresponding to $(001)_C$ or $(100)_C$, which established that the fine banding was the result of orthorhombic accommodation twinning. Dark field electron microscopy, using the various diffracted beams, shows that all adjacent bands contribute to the electron diffraction spots, indicating that alternate regions are crystallographically equivalent, but possess very small relative misorientations. A more complete discussion of orthorhombic twinning in this phase has been given elsewhere [10].

When selected area diffraction patterns were recorded from central regions of the plate, the repeating pattern of five spots indicated that the plane of the plate was parallel to a $(010)_O$ plane. Diffraction patterns recorded when the electron beam was translated to thin regions of the spine showed that here the crystal plane normal to the incident beam was a $(101)_O$ plane (fig. 4). Examination of such specimens at various angles of tilt confirmed that plate and spine were twin-related across a $\{110\}_C$ twin-composition plane. In addition, the observations indicate that a twin event has occurred at each spine-spine intersection.

A description of the crystallography of the $NaMgF_3$ phase in a complex-regular unit in terms of the cubic perovskite modification is similar to the morphological description given earlier, namely the spines have $\{110\}$ faces and intersect along a $\langle 111 \rangle$ direction with lamellar side-plates parallel to $\{100\}$ planes which is also the macrofacet plane. Twinning occurs when the crystal symmetry is reduced, the twinning planes at spine-spine and spine-plate intersections being
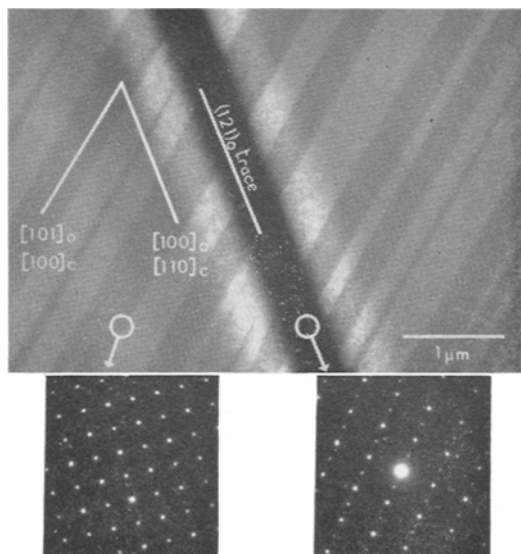

Figure 4 Transmission electron micrograph and corresponding selected area diffraction patterns from an extracted lamellar "side-plate" containing a portion of the connecting "spine".

$\{110\}_C$. The occurrence of twinning ensures that all side-plates have $[010]_O$ normals, as observed by electron diffraction.

The crystallographic orientation of the $NaMgF_3$ phase with respect to the macrofacet planes, is maintained during the lamellar to rod transition. Fig. 5 is a thin cleavage section parallel to the macrofacet plane in a region of rod morphology. The index of the macrofacet plane is $(101)_O$ and the diffraction pattern shows a section of reciprocal lattice which is orthogonal to that on the left of fig. 4, i.e. the $NaMgF_3$ is similarly oriented for both lamellar and rod morphologies. The visible twins in $NaMgF_3$ are of the same type as those in the lamellar plate of fig. 4. In fig. 5 the corresponding electron diffraction pattern for NaF indicates an apparent preference for the orientation relation: [110] NaF // $[101]_O NaMgF_3$ // Rod axis, $(1\bar{1}1)$NaF // $(12\bar{1})_O NaMgF_3$, but insufficient numbers of macrofacet sections were examined for confirmation of this relation.

4. Discussion

The "complex-regular" eutectic morphology has previously been observed in a number of systems in which one of the eutectic phases is usually an intermetallic compound of complex crystal structure or an element with mainly covalent bonding. These phases are assumed to
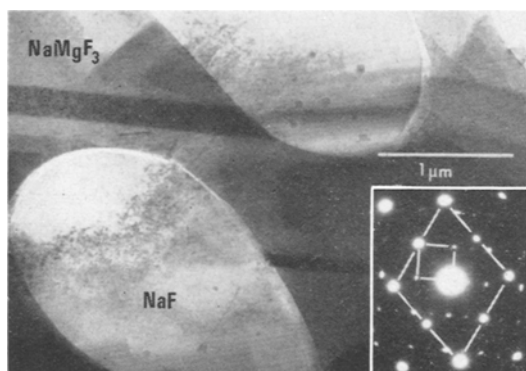
Figure 5 Transmission electron micrograph of a thin cleavage slice taken from the macrofacet plane in a grain with a rod morphology. The electron diffraction pattern includes reflections from the NaF rod phase (outlined by the diamond) and the $NaMgF_3$ matrix (outlined by the square).

be of the "faceted" type [1], such that an energy barrier exists for the addition of a new solid layer during solidification, which proceeds by the lateral movement of steps across a specific crystallographic "facet" plane. The growth rate is then determined by the rate at which these steps can form and involves a nucleation process on the facet plane. Examples of eutectics in which the "complex-regular" morphology has been observed are; $Zn-Mg_2Zn_{11}$ [11], Pb-Bi [12] and Al-Ge [13]. An understanding of the morphology of these eutectics requires explanations of the formation of macrofaceted cellular structures and the occurrence of coupled growth at the solid-liquid interface even when one expects the "faceted" eutectic phase to grow at a different degree of kinetic under-cooling from the non-faceted phase.

One of the few attempts to study the morphology and crystallography of these eutectics simultaneously has been made by Hellawell [13], for Al-Ge, and gives an explanation of the growth of the Ge phase in a coupled manner with Al, using information about the complex regular "triaxial unit" derived from X-ray analysis. He has demonstrated that twinning occurs at junctions between spines and between spines and lamellar side plates in the Ge phase. He postulated that the mechanism described by Wagner [14] and Hamilton and Seidensticker [15] operates at the location of these twinning events in this alloy, providing twin re-entrant edge sites which can continuously regenerate steps to feed the facet planes, thereby avoiding

the need for re-nucleation and enabling the faceted phase to advance at a lower kinetic undercooling. In consequence, it is possible to balance kinetic and solute undercoolings and provide an isothermal solid-liquid interface from which the regular morphology can develop. Since the twinning events in the $NaF-NaMgF_3$ eutectic are located at similar sites it is an attractive hypothesis that these events play an equivalent role in the growth process. However, operation of the $\{110\}_C$ tetragonal twinning mode would simply reflect one macrofacet plane into another, and therefore the Wagner mechanism cannot operate. An alternative hypothesis is that the tetragonal twins, like the orthorhombic twins, are nucleated after the eutectic has solidified. A small degree of tetragonality exists in the $NaMgF_3$ phase at the eutectic temperature. Distortion of the lattice increases progressively on cooling and may become sufficiently large to favour the nucleation of strain-accommodation twins. This distortion is, however, never as great as that for orthorhombic twinning, and would not require such numerous twinning events for compensation of lattice strain and such twins do not occur within plates or spines.

A further publication not based on observations in any particular system, but containing an adequate explanation of complex-regular morphologies, is that by Hunt and Hurle [8]. Firstly they suggest that the macrofacet cellular interfaces arise from the consequences of "faceted" phase behaviour. The formation of a microfacet in the solid/solid/liquid groove of a lamellar eutectic results in immobility of the groove and prevents rapid variations in the relative width of the two eutectic phases, which is necessary to accommodate compositional fluctuations. This will lead to the formation of a steep compositional boundary layer into which the macro-faceted cells project, in a manner similar to the impurity cell structures in eutectics where both phases are "non-faceted" but with planar macro-facets dictated by the crystallography of the "faceted" phase. Hunt and Hurle have also suggested that the development of microfacets at the ends of lamellar faults impedes their motion and hence prevents the lamellar space change mechanism necessary to accommodate growth fluctuations. The eutectic will then deviate from growth near to the "extremum" condition [16] and constitutional supercooling, with respect to one phase, will result if this deviation becomes large. Hurle and Jakeman [17], using pertur-

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bation theory, determine that an instability in the solid-liquid interface shape, of wavelength comparable with single phase cellular structures, results from impeding changes in the ratio of lamellar widths for the two phases. Their analysis, however, requires that the lamellar space change mechanism is not impeded, which is possible if the terminating lamellae are of the non-faceted phase. If this latter condition is not satisfied, irregular structures are expected [17]. The faceted phase in the NaF-NaMgF$_3$ eutectic deviates little from cubic crystal symmetry, particularly at the growth temperature, so that the orthogonal macrofacets may be considered as $\{100\}_C$ planes and originate because the dominant eutectic grains contain NaMgF$_3$ oriented with the fastest growing $\langle 111\rangle_C$ directions parallel to the macroscopic growth axis.

Hunt and Hurle have suggested that the regular structure on the macrofacet plane in complex-regular eutectics may be explained in a similar manner to the regular rod structures formed in certain "faceted"-"non-faceted" eutectics where the faceted phase forms the matrix. In the latter case one of the solid-liquid interface curvatures is concave when viewed from the liquid and microfacets cannot form on the "faceted" phase since a necessary condition for facet formation is that both curvatures must be convex at the point at which the interface is tangential to the low index facet plane. It is therefore proposed [8] that the interconnected morphology of the faceted phase in "complex-regular" eutectics provides regions of concavity at the solid-liquid interface for this phase. These regions may then feed the macrofacet plane and two-dimensional nucleation is avoided. It has also been pointed out that since the liquid groove angle is expected to be large, the probability of the region of convex curvature (on the faceted phase adjacent to the liquid groove) being tangential to a plane crystallographically equivalent to the macrofacet is small. Hence the mobility of the liquid groove is also maintained to provide for variations in relative widths of the solidifying phases. This will be valid for "faceted" phases of high crystal symmetry in which facet planes are of one form of low index. For the eutectic studied here the observed facet planes are orthogonal. The mechanism outlined above for the regeneration of surface steps in regions of concavity facilitates the coupled growth of "faceted" and "non-faceted" phases, but does

not explain the tendency for the lamellar morphology, extending from the spines in a "complex-regular" unit, to transform to a rod morphology in which the "faceted" phase forms the matrix. The transition is completed when the lamellar side-plates extend a certain distance away from the spine from which they are growing (figs. 1b and c). The extent of the rod morphology is clearly limited by the impingement of rods growing on adjacent macrofacets. When a grain in which the macrofacet plane is perpendicular to the ingot growth axis occurs with large cross-sectional area, the regular rod morphology is dominant (fig. 2). The process controlling the growth rate of the "faceted" phase is likely to be the lateral velocity of growth steps from the regions of concavity at the spine-lamellar junction. Hence it may be that at positions on the macrofacet remote from the spines the growth rate of the two phases perpendicular to the macrofacet differs sufficiently for an instability to occur at the triple junction between liquid and two solid phases. The formation of a rod morphology, in which the NaMgF$_3$ phase is a matrix, then provides a uniform distribution of positions with concave curvature to feed the macrofacet plane with growth steps. The mechanism for the transition from lamellar to rod morphology is obscure because one would logically expect the slowest growing (faceted) lamellae to be bridged by the "non-faceted" phase, which would then form a matrix. This configuration is unstable if the explanations of Hunt and Hurle are valid, since regions on the solid-liquid interface for the faceted (rod) phase contain only convex curvatures.

The formation of a regular rod morphology in which the rod phase occurs with a volume fraction near 0.5 is rare. For "non-faceted"/ "non-faceted" eutectics, rods are expected to form only if their volume fraction is less than 0.3 [17] and are not favoured until much lower volume fractions occur if solid-solid interfacial energies are anisotropic. It is possible that other eutectics involving "faceted"/"non-faceted" combinations could be induced to solidify completely with rod morphologies by seeding the orientation of the "faceted" phase such that the growth axis was normal to the macrofacet plane. The composite materials produced in this way would usually consist of a matrix of a mechanically more brittle phase threaded by more ductile rods of the "non-faceted" component present in large volume fraction.

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