

# Controlled Solidification of the Eutectic LiF-MgF<sub>2</sub>

M. W. A. BRIGHT, M. H. LEWIS

*School of Physics, University of Warwick, Coventry, UK*

A two-phase "model" composite material of LiF and MgF<sub>2</sub> has been prepared by unidirectional solidification of the mixed eutectic fluoride. The microstructure has been examined by optical and electron microscopy. The morphology is that of regularly arranged rods of the MgF<sub>2</sub> phase (rutile structure type) in a continuous LiF matrix. This microstructure is restricted to high purity materials with a planar solid-liquid interface and progressively degrades into a cellular lamellar structure associated with constitutional supercooling. The crystallographic orientation relation between the phases for the regular morphology has been determined as:

Growth axis             $//[001]\text{MgF}_2//[001]\text{LiF}$ ,  
Preferred interfaces  $//(110)\text{MgF}_2//(100)\text{LiF}$   
and  $(1\bar{1}0)\text{MgF}_2//(010)\text{LiF}$ .

## 1. Introduction

The research described in this paper forms part of a systematic study of the microstructure and mechanical properties of "model" composite materials prepared by unidirectional solidification of mixed fluoride eutectics. In part of this research the two phases constituting the eutectic structure are characterised by crystal structures of cubic symmetry which solidify with a regular lamellar morphology (LiF-NaF, LiF-CaF<sub>2</sub>). In the system LiF-MgF<sub>2</sub> described here, the crystal structures of the eutectic phases have cubic and tetragonal symmetry, respectively. When solidification occurs under conditions of planar solid-liquid interface from a high purity melt, regular aligned rods of MgF<sub>2</sub> (rutile structure type) form in a matrix of LiF (rock salt structure type). The development of this morphology and conditions under which a degradation of the regular structure occurs are described here.

## 2. Experimental Techniques

### 2.1. Solidification

Lithium fluoride and magnesium fluoride, in fine powder form, were mixed together and melted in a wire wound resistance furnace in graphite moulds 18 cm long and 7 mm internal diameter. The moulds were encased in stainless steel tubes to reduce oxidation of the graphite. Porosity, arising from entrapped gases, was eliminated by

adding the charge in small quantities, so that the powder melted in the liquid meniscus, and subsequently maintaining the samples at 830°C for a period of 24 h. The ingots were then transferred to a Bridgman-type crystal growth furnace incorporating a silicon carbide heating element and were unidirectionally solidified by downward withdrawal of the crucible through a temperature gradient of 40°C cm<sup>-1</sup> from an initial temperature of 820°C. Temperature gradients were recorded by a thermocouple in the melt. Specimens were solidified at rates from 0.1 to 10 cm h<sup>-1</sup>.

Specimens were prepared with compositions of LiF and MgF<sub>2</sub> expressed in mol %, (LiF-MgF<sub>2</sub>), in the range from (80-20) to (60-40) and it was found that a starting composition of (70-30) approximated closest to eutectic composition after subjection to the sequence of heat treatments described above. Initial experiments were performed using nominally > 99.5% pure laboratory grade reagents. Effects arising from constitutional supercooling were eliminated from all but the last centimetre of the specimen length in more recent work using "Optran" grade reagents supplied by BDH Ltd.

### 2.2. Microscopy

Sections for optical microscopy were cut with a diamond saw, mounted in plastic and polished

through grit papers to 1  $\mu\text{m}$  diamond paste before etching in dilute nitric acid.

Particular use was made of a JEM 200 electron microscope in a determination of the crystallographic relation between eutectic phases. Specimens were prepared either by extracting rods of the MgF<sub>2</sub> rich phase, using dilute ammonia solution, or cleaving fragments from longitudinal surfaces such that both phases could be examined simultaneously. Good quality electron diffraction patterns and images could be recorded from sections between 1.5 and 2  $\mu\text{m}$  in thickness and a marked increase in stability of the phases, when exposed to the 200 kV electron beam, over that at 100 kV, was apparent.

Scanning electron microscopy was used to obtain better resolution of microstructure on polished and etched surfaces and for establishing continuity of the minor phase. Specimens were coated with a carbon film to prevent charging of the surface in the electron beam.

### 3. The Eutectic Microstructure

The observed microstructures in the unidirectionally solidified ingots may be divided into three types for convenience of presentation; an initial region containing many small randomly oriented "grains" and sometimes primary phase (depending on the melt starting composition); a central region, where the solid-liquid interface was planar, composed of a few "grains" of rod-like eutectic aligned parallel to the growth direction and a final region where the planar interface had become unstable and resulted in impurity cell formation.

#### 3.1. Growth Under Planar Interface Conditions

##### 3.1.1. Growth morphology and phase composition

Melts made from high purity components which were solidified at rates  $< 1 \text{ cm h}^{-1}$  contained large grains ( $> 2 \text{ mm}$  diameter) with a rod morphology over several cm of growth (fig. 1). Analyses based on relative interfacial areas for a given volume fraction and constant phase spacing indicate that a rod morphology should be stable, if the volume fraction of one phase is less than 0.28 to 0.32 [1, 2], but the lamellar morphology should form for higher volume fractions. The volume fraction measured on transverse sections of the LiF-MgF<sub>2</sub> eutectic was 0.42. An explanation of this anomaly may be given in terms of the phase diagram for this

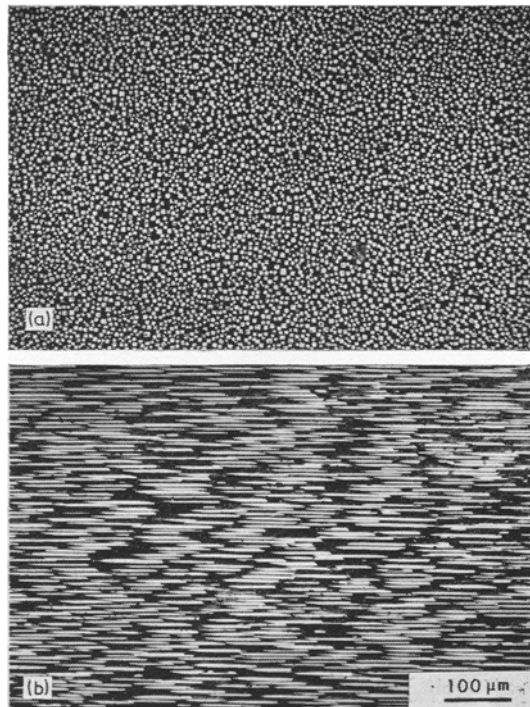


Figure 1 Optical micrographs of (a) transverse and (b) longitudinal sections through a single eutectic "grain" after unidirectional solidification at  $10 \text{ mm h}^{-1}$ .

system (fig. 2a). From this diagram a plot of volume fraction versus undercooling (below the eutectic temperature) was made (fig. 2b). It is observed that for small undercoolings the volume fraction may fall below the limiting value of 0.28 for which the rod morphology is preferred over the lamellar morphology. For an undercooling of  $20^\circ\text{C}$  the composition of the two phases is far removed from that of the pure components due to their large mutual solid solubility. At room temperature, however, there is limited solubility of one fluoride in the other. It is therefore envisaged that the eutectic grows at an undercooling of  $\leq 20^\circ\text{C}$ , with a volume fraction favouring a rod morphology. On subsequent heat treatment, during cooling to room temperature, the excess LiF and MgF<sub>2</sub> in the MgF<sub>2</sub>-rich and LiF-rich phases, respectively, diffuses to the rod-matrix interface, resulting in a movement of the rod-matrix boundary and a subsequent increase in volume fraction towards the room temperature equilibrium volume fraction of 0.49. Electron imaging and scanning for Mg<sub>k $\alpha$</sub>  X-rays with an electron probe microanalyser, on polished sections of the eutectic, confirmed that the minor

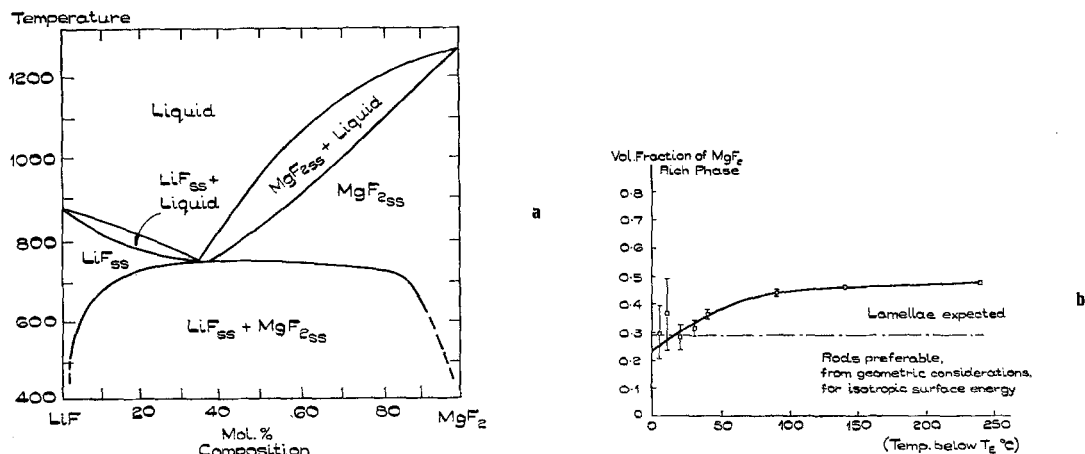


Figure 2 (a) Phase diagram for the system LiF-MgF<sub>2</sub>. The LiF rich solidus and liquidus curves cannot meet at the eutectic point but appear to do so on the diagram which is redrawn from [3]. (b) Predicted phase volume fraction as a function of undercooling below the eutectic temperature T<sub>E</sub>. The data points have been derived from fig. 2a, on the assumption of phase compositions determined by the equilibrium solvus and hence are subject to greater uncertainty near the eutectic temperature.

phase was predominantly MgF<sub>2</sub>. It was not possible to detect MgF<sub>2</sub> in the LiF-rich phase. Debye-Scherrer X-ray photographs of the grown eutectic and the starting materials were indistinguishable. Thus, it is established that the major phase of the eutectic is predominantly LiF and the minor phase predominantly MgF<sub>2</sub>.

### 3.1.2. Crystallographic orientation relations

The orientation relation between LiF and MgF<sub>2</sub>-rich phases was determined first for the very large grains which represent the preferred orientation relation and interface planes. In these grains the MgF<sub>2</sub> rods were of square cross-section. Hence, the crystallographic relation between the two phases should be given as:

(i) a statement of crystallographic planes in both phases which are parallel and form interface planes:

(ii) a statement of parallel directions in the two phases, which preferably should be the eutectic growth direction and be contained within the quoted interface planes.

This was accomplished in part by the Laue back reflection X-ray technique, on a transverse section from which it could be stated:

Growth axis // [001] LiF // [001] MgF<sub>2</sub>  
 Interface planes //(100) LiF //(100) or  
 (110) MgF<sub>2</sub>

Since the rods have a square cross-section a second interface is //(010) LiF //(010) or (1 $\bar{1}$ 0)

MgF<sub>2</sub>. The ambiguity in indexing the interface planes arises from the small spread in orientation ( $\pm 2^\circ$ ) and hence in Laue spots due to the tetragonal MgF<sub>2</sub> phase.

Confirmation of these relations, together with an elimination of the ambiguity in interface plane, was provided by electron diffraction. Fig. 3a illustrates superimposed diffraction patterns for the two phases which contain the growth axis and an interface plane normal. The scatter in MgF<sub>2</sub> orientation obtained by observing Kikuchi electron diffraction patterns on traversing 10 to 20 rods in the longitudinal thin section did not exceed  $2^\circ$ . This represents a random directional deviation consistent with the X-ray orientation analysis where the X-ray beam typically selects an area of 1 mm<sup>2</sup>.

The preferred orientation relation was therefore established as:

Growth axis // [001] LiF // [001] MgF<sub>2</sub>  
 Interface plane //(100) LiF //(110) MgF<sub>2</sub>  
 and //(010) LiF //(1 $\bar{1}$ 0) MgF<sub>2</sub>

When the preferred growth axis and orientation relation is maintained secondary interfaces are infrequently observed such that (100) LiF // (100) MgF<sub>2</sub> and (1 $\bar{1}$ 0) LiF // (010) MgF<sub>2</sub>, making angles of  $45^\circ$  with those of the primary interfaces in transverse section.

Deviations from the preferred crystallographic relations in excess of a 2 to  $3^\circ$  result in small modifications in the morphology of the MgF<sub>2</sub>

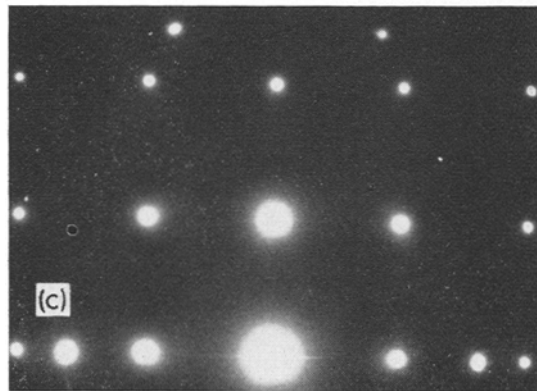
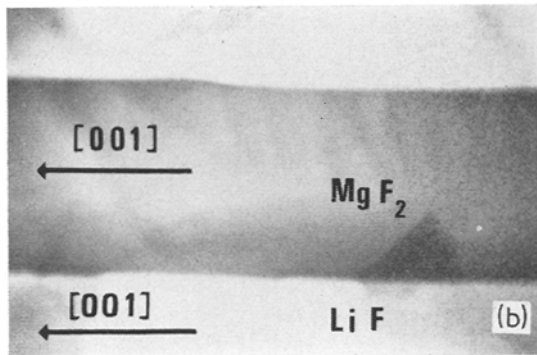
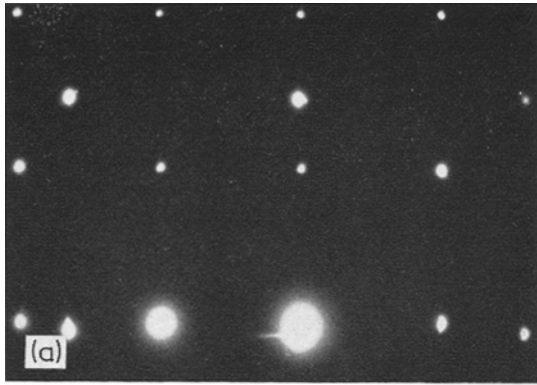


Figure 3 (a) Selected area electron diffraction pattern from adjacent regions of LiF and MgF<sub>2</sub> phases in the region of regular rod morphology. The patterns correspond to (010)\* LiF and (1 $\bar{1}$ 0)\* MgF<sub>2</sub> reciprocal lattice sections. (b) Corresponding thin section in correct orientation relative to the diffraction pattern. (c) Diffraction pattern from a two phase regular region of round section rods demonstrating the rotation of LiF, with respect to MgF<sub>2</sub>, about the growth axis. The patterns correspond to (130)\* LiF and (1 $\bar{1}$ 0)\* MgF<sub>2</sub> reciprocal lattice sections.

rich phase. A small rotation of [001] LiF about axes perpendicular to the preferred interface

MgF<sub>2</sub> rod cross-section such that one pair of parallel interfaces of the preferred type are retained. The second parallel pair which now deviate from the preferred interface crystallography have increased energy and are suppressed in development during growth and post-solidification cooling (fig. 4)

A relative rotation of the MgF<sub>2</sub> and LiF

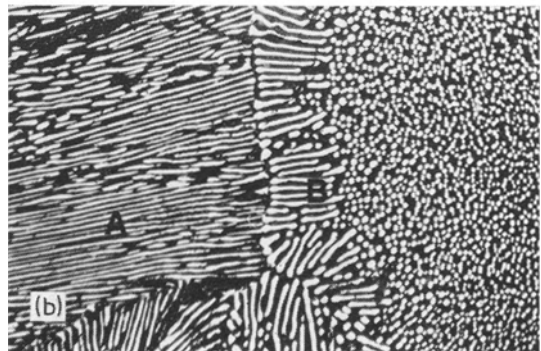
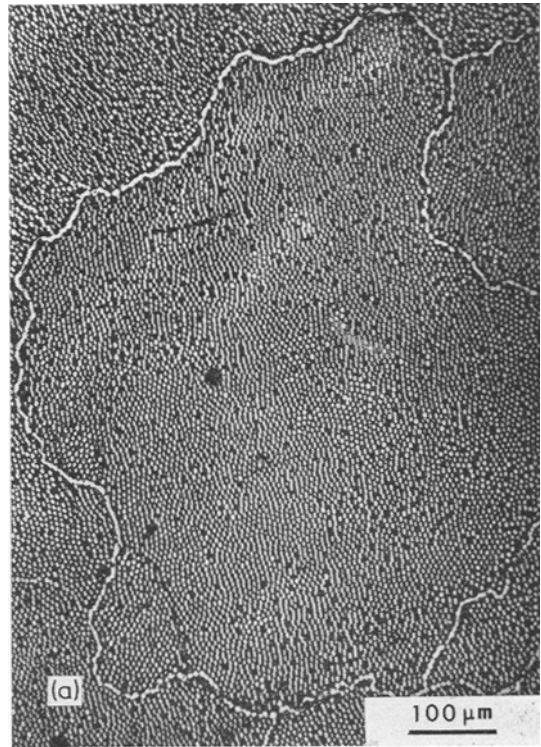


Figure 4 (a) Transverse section of large eutectic "grains" with small relative rotations about the growth axis. (b) Transverse section from a region containing smaller eutectic grains of large misorientation.

structures about the [001] growth axis, detected in a few grains by electron diffraction (fig. 3c), results in a destruction of the quoted interface plane relation and the formation of nearly round section rods. This modification in orientation relation presumably results in near equality of interfacial energy for all planes with [001] zone axes.

More extreme microstructural variations occur in the early stages of ingot solidification, involving small outgrowing grains containing a lamellar morphology. The extremely small grain size at this stage precluded their selection for analysis by electron diffraction.

### 3.2. Growth Under Non-Planar Interface Conditions

#### 3.2.1. Grain boundaries

A distinction is made here between grain boundaries typically observed between large grains in which the preferred phase orientation relation occurs and those in which a large angular misorientation exists between the LiF matrix on either side of the boundary. The first type consist of tilt boundaries, usually due to small relative rotations about the [001] LiF growth axis resulting in low boundary energies and a retention of the stable rod morphology adjacent to the boundary. They are delineated in transverse section (fig. 4a) by a preferential thickening of the  $\text{MgF}_2$  phase during post-solidification cooling resulting from enhanced grain boundary diffusion. Boundaries of the second type occur near to the initial solidification zone which contains some smaller grains with non-preferred growth axes. Two microstructural features of importance which develop under these conditions are illustrated in fig. 4b. Firstly, the relatively small grain (A) contains  $\text{MgF}_2$  in lamellar form believed to arise from stabilisation of a relatively low energy lamellar interface which does not contain the preferred growth axis. Secondly, the latter grain is surrounded by grains (B) which have near preferred orientations such that they contain  $\text{MgF}_2$  in rod form but which degrades into irregular lamellar form adjacent to the high angle boundary. The lamellae apparently form due to a curvature of the solid-liquid interface near to the boundary, such that the growth axis deviates locally from [001] LiF. The origin of this local curvature may be in the cusp produced on the solid-liquid interface when intersected by a high energy grain boundary or in the establishment of a small lead distance for the preferred

orientation eutectic grain over the smaller grains growing with larger undercooling. The  $\text{MgF}_2$  rods cannot deviate from their preferred growth direction without the formation of a new interface relation, as required for the changed direction of solid-liquid interface motion in the region of curvature. Hence, they meet the solid-liquid interface obliquely and extend laterally when the liquid adjacent to the boundary solidifies.

#### 3.2.2. Cellular interfaces

Following approximately 5 cm of growth, for the high purity eutectic, constitutional supercooling arising from the build up of impurities stabilises cellular projections on the advancing solid-liquid interface. For a small degree of supercooling, the interface is nearly planar in the cell centres, but curved near the cell boundaries. The  $\text{MgF}_2$  rods in boundary regions broaden into lamellae in the manner described above for grain boundaries whereas rods in the cell centre are unchanged (fig. 5a). Further development of impurity cells result in lamellar broadening throughout the cell cross-section (figs. 5b and c). The lamellar interfaces developed via this mechanism show a preference for radial growth such that three of the four original rod interface types (100) LiF // (110)  $\text{MgF}_2$  and (010) LiF // (1 $\bar{1}$ 0)  $\text{MgF}_2$  are retained. A secondary preference for alternative interfaces of the type (110) LiF // (100)  $\text{MgF}_2$  or (110) LiF // (010)  $\text{MgF}_2$  (as occasionally observed for rods under planar interface growth conditions) was observed.

## 4. Discussion

### 4.1. The Preferred Growth Morphology and Orientation

It has been demonstrated that regular aligned microstructures associated with coupled growth of phases constituting the eutectic is possible in the system LiF- $\text{MgF}_2$ . The occurrence of a rod morphology for the  $\text{MgF}_2$  phase has been explained in part by the assumption that the average undercooling at the planar solid-liquid interface does not exceed 20°C and that the simple analysis of minimum interfacial area for rods (when the phase volume fraction is less than 0.28) is applicable. This analysis assumes isotropy of interfacial energy, a situation which occurs infrequently, and in view of the observation of square rod cross-sections, the nature of possible interfaces between the eutectic phases should be examined.

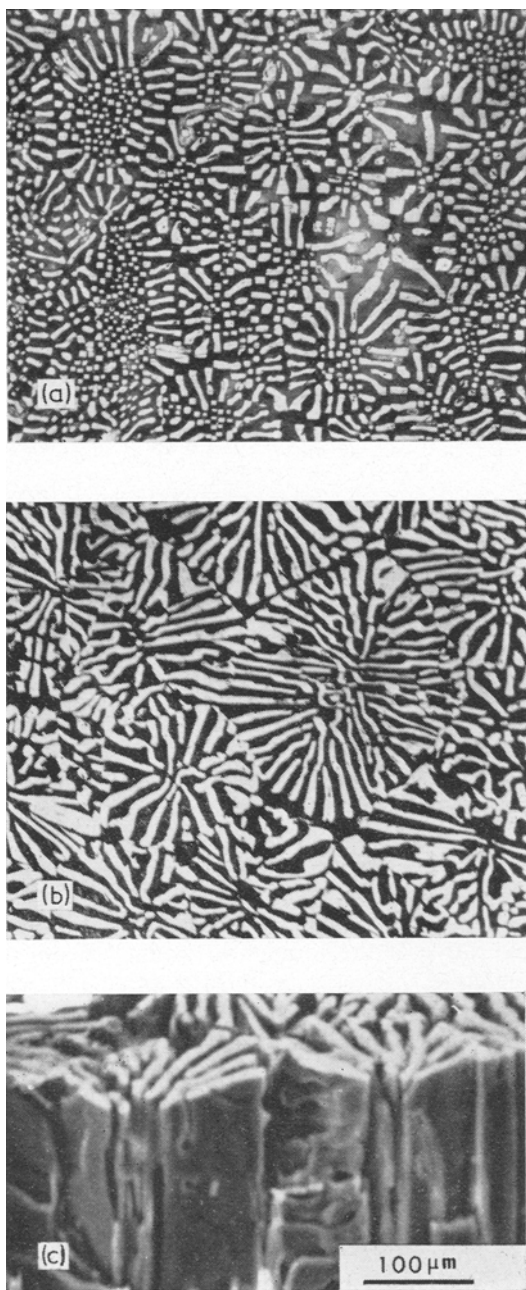


Figure 5 Transverse sections through regions containing impurity "cells", (a) soon after the onset of constitutional supercooling; (b) an advanced stage in degradation of the rod morphology; (c) the structure in (b) revealed by scanning electron microscopy after removal of the LiF matrix phase.

In a search for possible low energy interfaces between phases it is necessary to identify crystal-

lographic planes in the two structures which have a similar symmetry and ion spacing. An important factor for structures with predominantly ionic bonding is that charge neutrality for groups of ions adjacent to the interface be maintained, i.e. Pauling's second rule [4] for ionic structures is satisfied. This factor is likely to assume importance when the two structures contain ions of different valence (e.g. Li and Mg). This analysis may be assisted by experimental observations of precipitation of the minor phase, in the matrix phase in which the precipitate habit is frequently determined to be a plane of small mismatch for the two structures and hence of low energy. In the system LiF-MgF<sub>2</sub> there is appreciable mutual solubility of the components, resulting in a small miscibility gap near the eutectic temperature which rapidly increases with decreasing temperature (fig. 2a). Precipitation of the equilibrium MgF<sub>2</sub>-rich phase in a LiF matrix has previously been studied by Lilley and Newkirk [5] with orientation and interface relation:

Interface  $\parallel(100) \text{ MgF}_2 \parallel(111) \text{ LiF}$ , and  
 $[001] \text{ MgF}_2 \parallel[1\bar{1}0] \text{ LiF}$

Their analysis of this observation is based on the similarity in ion distribution in both phases for the given interface planes when aligned with the observed directions parallel. The precipitate particles are large, plate shaped and follow the precipitation of smaller intermediate (metastable) precipitates such that the choice of plate habit is likely to be dominated by the requirement for minimum interfacial energy and not by anisotropy in elastic modulus which may be important for small coherent particles. An analysis of the conditions for co-ordination of ions in the two structures adjacent to such an interface further substantiates the claim that this orientation relation results in a low energy habit plane. The exposure of a  $\{111\}$  LiF surface results in a planar array of either F<sup>-</sup> ions or Li<sup>+</sup> ions with a charge imbalance of  $e/2$  per ion, i.e. 3 "bonds" between positive and negative ions constituting each octahedral group, are unsatisfied, each having a "bond strength" (cation co-ordination/cation valency) of  $e/6$ . Charge neutrality at this surface may be achieved by placing a (100) MgF<sub>2</sub> cation plane in contact with a LiF anion plane. For (100) MgF<sub>2</sub>, three unsatisfied bonds, forming part of an octahedral group, result in an excess charge of  $e$  per cation, the "bond strength" in this case being  $e/3$ . Since the number of ions per unit area of interface plane for MgF<sub>2</sub> is one half that for (111) LiF the net charge associated

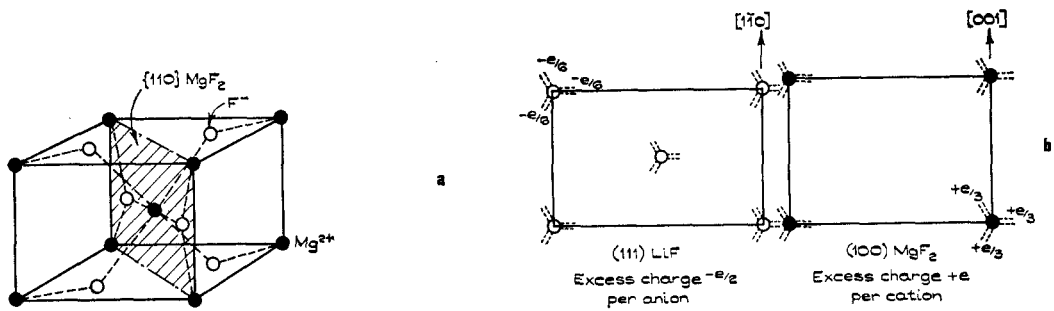


Figure 6 (a) The distribution of ions in a unit cell of the  $\text{MgF}_2$  structure. (b) A comparison of distribution and excess charge for ions in  $\{111\}$  LiF and  $\{100\}$   $\text{MgF}_2$ .

with this interface is zero. This is illustrated in fig. 6, in which a  $\{111\}$  LiF anion plane and  $\{100\}$   $\text{MgF}_2$  cation plane are compared. A similar comparison for other possible interfaces, of high ion density in the two structures, fails to reveal a comparable relation, suggesting that the observed precipitate interface corresponds to that of minimum energy, i.e. the equilibrium interface. It is pertinent therefore to compare the precipitation mode for interface formation with that for unidirectional eutectic solidification.

It is believed that the most important difference between the two processes is the absence, in the case of precipitation, of the constraint arising from a preferred growth from the liquid of one or both phases in a particular crystallographic direction. It has been observed that the retention of a regular  $\text{MgF}_2$  rod morphology is restricted to grains in which the growth axis is near  $\langle 001 \rangle$  LiF //  $\langle 001 \rangle$   $\text{MgF}_2$ . These directions must therefore be contained within any developing solid-solid interface, which is clearly inconsistent with the equilibrium (precipitate) interface for the LiF phase. It is suggested that eutectic grains with the quoted growth axis grow ahead of others at the solid-liquid interface, corresponding to a smaller undercooling required for growth. This implies that the kinetic undercooling, normally neglected in analyses of solidification in regular metallic eutectics, is dominant over the requirement for a reduction in undercooling by selection of the equilibrium solid-solid interface orientation. Coupled growth of the two phases is maintained if the component of kinetic undercooling is similar for both phases and growth occurs under a large temperature gradient at the solid-liquid interface.

The observation of the choice of an  $\langle 001 \rangle$  growth direction for the LiF-rich matrix phase is surprising in view of the variety of preferred growth directions reported for simple eutectic systems composed of phases with "rock salt" structures, normally  $\langle 110 \rangle$  or  $\langle 100 \rangle$  [6-8]. However, in this system LiF contains a high concentration of  $\text{Mg}^{2+}$  ions and constitutional vacancies at the growth temperature which may induce a marked anisotropy in interface attachment kinetics.

The two phases, in addition to the adoption of highly preferred growth axis, exhibit a preferred crystallographic orientation relation with respect to relative rotations about these axes. This is indicative of the formation, during growth, of preferred interfaces in an attempt to minimise interfacial energies. The symmetry of both structures about the growth axis is consistent with the development of equiaxed rod cross-sections. The preference for the observed interfaces is not readily explicable in terms of simple interface matching criteria of the type described above. Ion distributions on the mating planes are markedly dissimilar and attempts to rationalise the adjacent charge distributions do not produce a convincing explanation for this interface preference.  $\{100\}$  LiF planes consist of alternating sequences of positive and negative ions which results in average charge neutrality.  $\{110\}$  or  $\{1\bar{1}0\}$   $\text{MgF}_2$  planes have excess surface charge regardless of planar section in the unit cell (fig. 6a). These matching criteria must, however, contain an over-simplification since the interface structure and charge balance will be modified by the high mutual solubility of components at the growth temperature.



The preference for growth axes in both structures with four-fold symmetry is important in the exclusion of a lamellar morphology. Any rotational orientation relation about this axis may result in orthogonal interfaces of equivalent energy and preclude the formation of a singular lamellar interface. The condition dictated by total interfacial area for a fixed phase spacing must additionally be satisfied, that is, a volume fraction for the MgF<sub>2</sub>-rich phase of less than 0.3 at the growth temperature.

#### 4.2. Development of the Eutectic Microstructure

Following the explanation given above for the microstructure observed in grains of preferred growth axis under planar interface conditions, a brief description will be given of a possible sequence for its development and subsequent degradation.

Unseeded nucleation of eutectic grains in random orientation occurs at the tip of the graphite container. Epitaxial nucleation of the MgF<sub>2</sub>-rich phase within LiF probably occurs according to the equilibrium orientation relation, derived for the precipitation process, in all initial grains. Those grains having growth axes near to  $\langle 100 \rangle$ LiF are selected for preferential growth because of the smaller degree of undercooling required for their advance. The MgF<sub>2</sub>-rich phase may undergo a progressive re-orientation or be selected from randomly oriented nuclei to adopt the [001] growth axis. Grains containing MgF<sub>2</sub> with non-preferred axes of growth may degenerate into an irregular morphology if the MgF<sub>2</sub> phase trails the LiF phase at the solidification front and the stability of the triple junction between two phases and the liquid is destroyed, i.e. the condition of coupled growth for the eutectic phases is restricted to solid-liquid interfaces for which MgF<sub>2</sub> or LiF have the preferred growth axis. When both phases adopt their preferred growth axes, the rod morphology is permitted according to the description given above. The mechanism for the suppression of grains with non-preferred growth axes is that of radial expansion of the preferred grains which advance at smaller undercooling. This mechanism requires a progressive increase in the number of MgF<sub>2</sub> rods as the area of preferred grains in transverse section increases. This is accomplished by a rod branching process resulting in "tree-like" configurations. These have been observed by scanning electron microscopy after chemical

dissolution of the LiF phase.

MgF<sub>2</sub> rods undergo additional crystallographic rotations about the growth axis to achieve the preferred interfaces. Eutectic grains, characterised by the preferred orientation relation, interface planes and growth direction, continue to grow at the expense of the remaining smaller grains of non-preferred growth direction with a resultant microstructure exemplified by fig. 4a. At this stage a number of large grains are stable, having relative rotations about the growth axis. In some ingots one grain characterised by exactly square section rods of the MgF<sub>2</sub>-rich phase, and therefore closest to the preferred growth axis, grows to a size which occupies a large proportion of the ingot cross-sectional area. This process occurs slowly and is often precluded by the onset of constitutional supercooling.

The structural modification accompanying constitutional supercooling results from the inability of MgF<sub>2</sub> rods to follow the local variations in growth direction at the non-planar interface. Hence, the rod morphology degrades into that of non-parallel lamellae radiating from the apex of the domed solid-liquid interface of the impurity cell by the mechanism described previously.

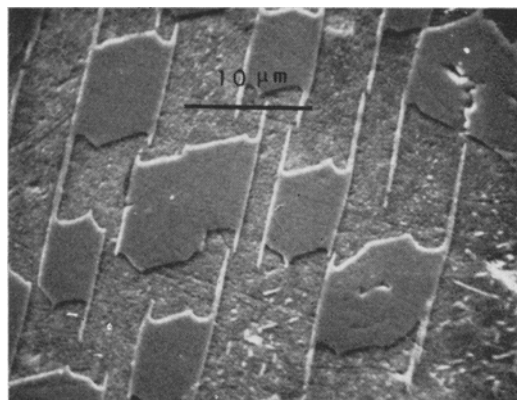


Figure 7 Plate shaped side growths, on misaligned rods of MgF<sub>2</sub>, formed during post-solidification cooling.

Following the growth sequence, an adjustment in phase composition and volume fraction occurs during cooling from the solidification temperature. Growth of the MgF<sub>2</sub>-rich phase occurs, at the expense of the LiF-rich phase in preferred grains without modification of the relatively low energy interface such that square section rods retain this shape. For other grains which deviate



from the preferred growth axis, the shape deviation of rods from four-fold symmetry in transverse section is accentuated by a continued preference for growth parallel to the elongated interface of lower energy. An extreme example of this process occurs in small outgrowing grains in which elongated pseudo-lamellae develop thin plate-shaped side growths retaining an interface and orientation believed to conform with that observed for precipitation (fig. 7). In some ingots the super-saturation for the  $MgF_2$  phase is sufficient for the nucleation and growth of plate-shaped precipitates between the  $MgF_2$  phase formed by eutectic reaction.

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### References

1. F. C. FRANK and K. E. PUTTICK, *Acta Metallurgica* **4** (1956) 206.
2. K. A. JACKSON and J. D. HUNT, *Trans. AIME* **236** (1966) 1129.
3. W. E. COUNTS, R. ROY, and E. F. OSBORN, *J. Amer. Ceram. Soc.* **36** (1953) 12.
4. L. PAULING, *J. Amer. Chem. Soc.* **51** (1929) 1010.
5. E. LILLEY and J. B. NEWKIRK, *J. Mater. Sci.* **2** (1967) 567.
6. J. W. MOORE and L. H. VANVLACK, *J. Amer. Ceram. Soc.* **51** (1968) 428.
7. P. TRUELOVE, D. DOUBLE, and A. HELLAWELL, *J. Cryst. Growth* **2** (1968) 191.
8. M. W. A. BRIGHT, Ph.D. Thesis, University of Warwick (1970).

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