5.1 Introduction

This chapter discusses in detail the morphology of the observed forms of crystallographically oriented precipitates of BaCl₂. The idealized morphology is shown to be consistent with the supposed orientational relationships. In § 5.4 we shall discuss the questions of the energy and structure of the hetero-crystalline interfaces generated between the contact planes of precipitate and matrix. The discussion will be in the light of current concepts in the theories of interfacial energies (§ 4.5). As both of the materials involved are ionic, questions involving possible excess electrostatic charge at the interfaces will also be examined. The interface structure proposed in § 5.5 is consistent with the assumed degree of coherency of the interfaces in the case of platelets in the cubic phase (viz H-I, O-I, D, Rh, etc) and the requirement that close packing be preserved when approaching an interface from either side.

The precipitates exhibit two principal types of morphology, viz rods and platelets. The morphological transition (rod → platelet), if there is any, depends upon factors such as solute supersaturation, working temperature, direction of maximum solute supply etc. By imposing specific conditions of temperature and of environment for nucleation and growth to occur within the crystal the rod- and/or
platelet-shape could be induced. The dispersion of precipitates of one or the other type (or both) in the matrix has tremendous influence on the age-hardening properties of crystals of NaCl-BaCl$_2$ analogous to alloy systems such as Al-Cu (§ 2.12). The exact details of crystallographic orientation of rods and/or platelets are expected to be determined by the crystal structures of matrix and precipitate, by the surface energy anisotropy of the precipitate structure and also by the matrix-precipitate interfacial energy.

As the finer details of the shapes of rods are not resolved in the optical microscope no discussion on the structure and energy of rod-matrix interfaces has been attempted. There is just not enough information. Similarly, the interfaces between non-cubic BaCl$_2$-platelets and matrix have not been examined. The information available so far is insufficient to identify the non-cubic phase exactly. Non-cubic BaCl$_2$ can exist as hydrated (BaCl$_2$ $\cdot$ H$_2$O or BaCl$_2$ $\cdot$ 2H$_2$O) or unhydrated salt. The structure can be orthorhombic or monoclinic. Hence the discussion is confined to interfaces between platelets in the cubic phase and matrix. Cubic BaCl$_2$ has fluorite structure (a$_0$ = 7.34 Å). The precipitates in the non-cubic phase are discussed as to general morphology only.

5.2 Rod-like Precipitates

Rods R-I, R-II, R-III have similar morphological character, viz they are thin and long, and they are parallel to simple crystallographic directions in the matrix. Towards their
ends there are small but significant differences (Figures 2.4-2.6, 2.8).

Of these, only R-I are what may be termed 'true rods', because they are seen as rods no matter in what matrix crystallographic direction they are observed (\(<100>^\text{m}, <110>^\text{m}, <111>^\text{m}\)). The material of these rods is cubic BaCl\(_2\). However R-II and R-III lying parallel to \(<100>^\text{m}\) and \(<110>^\text{m}\) respectively are non-cubic. Further, they appear as rods only when viewed along \(<100>^\text{m}\) and \(<111>^\text{m}\) respectively. Based on the differences in shape at the ends (and on observations in polarized light) it is concluded that they are nothing but 0-II and H-II respectively, viewed edgewise. This conclusion and their optical character are compatible with the observed morphology of non-cubic platelets. The blunt, rounded appearance of the ends of R-II is also due to an optical effect when 0-II are observed edgewise. Dark-field observations along \(<100>^\text{m}\) and \(<111>^\text{m}\) make it clear that a long and pointed R-III rod is nothing but an H-II hexagonal platelet seen along \(<111>^\text{m}\). An H-II platelet, shown as having \(\{hkl\}\)-planes in Table 2.1 is in its turn nothing but two platelets lying in two different \(\{112\}\) with their common section parallel to \(<110>^\text{m}\) (Figures 2.11b, 2.14a, 2.19c). This is seen quite clearly when observations are made along \(<001>^\text{m}\). This could be a twinned BaCl\(_2\)-platelet in the non-cubic phase.

5.3 **Polygonal Platelets**

Platelets H-II (non-cubic) were considered in § 5.2 above in the context of rods R-III. No further reference will be made to
Fig 5.1 Showing various directions on \((111)_m\). The numbers from 1 to 6 denote \(\langle 123 \rangle_m\).
them. In this section we discuss the morphology of cubic platelets H-I, O-I, D, Rh (Figure 2.29 and Table 2.1). All these are incredibly sharp, and regular or semi-regular. As they are embedded in another cubic structure, \textit{viz} NaCl, with planes parallel to \{111\}_m it may be inferred that \{111\}_{\text{BaCl}_2}-planes are parallel to \{111\}_{\text{NaCl}}-planes. The hexagonal symmetry of H-I is also indicative of the same. The stacking of \{111\}-planes in the NaCl-structure consists of alternate \textit{Na}^+ and \textit{Cl}^--planes. The detailed stacking sequences will be discussed in §5.5. Suffice it here to remark that the matrix plane adjacent to the terminating plane of a platelet can be a \{111\}-plane, either \textit{Na}^+ or \textit{Cl}^--ions.

Figure 5.1 is a schematic drawing showing the lattice sites on a \{111\}_m-plane and also showing various matrix directions. For the sake of convenience in discussion the six \textit{<123>}-directions are denoted by numbers from 1 to 6. All of the platelets have their sides parallel to \textit{<123>}_m as established from back-reflection Laue analysis. From the known lattice parameters of NaCl (5.63 Å) and \textit{BaCl}_2 (7.34 Å) we see by inspection that the interionic distances in the two are related as

\[
| <123>_{\text{NaCl}} | = 2 | <110>_{\text{BaCl}_2} |
\]  

(5.1)

Taking all of this into account we now assert that the orientational relationships between matrix and platelets is the following:

\[
\{111\}_{\text{NaCl}} \parallel \{111\}_{\text{BaCl}_2}
\]

\[
<123>_{\text{NaCl}} \parallel <110>_{\text{BaCl}_2}
\]  

(5.2)
Fig 5.2 Two possible orientations of a hexagonal platelet parallel to \((111)_m\). The lines inside and outside the platelets are parallel to \(\langle 110 \rangle_p\) and \(\langle 110 \rangle_m\) respectively.
and that the platelets are coherent with \{111\} \text{NaCl}.

5.3.1 **Hexagonal Platelets H-I** (Figures 2.1, 2.9-2.12, 2.15-2.18)

These platelets have two distinct orientations in a given \{111\}_m-plane. In each the sides are parallel to \langle 123\rangle_m. In terms of platelet structure the platelet-plane is \{111\}_p and the sides are parallel to \langle 110\rangle_p. The very interesting fact of two distinct but crystallographically equivalent orientations can be understood as follows. On a given \{111\}_m there are six \langle 123\rangle_m. In Figure 5.1 these are denoted by numbers from 1 to 6. Figure 5.2 is a schematic drawing showing the idealized morphology of the two possible ways in which regular hexagonal platelets without re-entrant corners can be formed. The horizontal and vertical boundaries of the frame are parallel to \langle 110\rangle_m and \langle 112\rangle_m respectively. The lines of the nets drawn inside and outside the hexagons are parallel to \langle 110\rangle_p and \langle 110\rangle_m-directions respectively. The intersections of lines denote ionic positions in the respective structures. This figure shows essentially two important geometric features on the basis of which the interface structure will be evolved in §§ 5.4-5.5. This is also the basis on which the idealized morphology of other platelet forms can be understood. The essential feature of Figure 5.2 is that it can represent a surface common to \{111\}_m and \{111\}_p which is the situation at a terminating plane of a platelet; say, it represents the bottom surface of a platelet. The geometry of the top terminating plane will be identical except for lateral displacements appropriate to the structure (and, of course, except for the kind
Fig 5.3(a) Three possible orientations of an octagonal platelet parallel to $(111)_m$. The lines inside and outside the platelets are parallel to $<110>_p$ and $<110>_m$ respectively.
of ions). Considering for the moment the bottom surface of a platelet to be represented by Figure 5.2 the positions of ions in the \(\{111\}_p\)-layers above it and those in the \(\{111\}_m\)-layers below it can be imagined.

5.3.2 Octagonal Platelets 0-I (Figures 2.19, 2.21-2.22)

The morphology exhibited by these platelets also is interesting. These are invariably semi-regular with sides parallel to \(<123>_m\) belonging to both sets on a given \((111)_m\). On a given \((111)_m\) there are, in all, three orientations. The considerations of § 5.3.1 are applicable to these platelets also. Similarly, the morphology is compatible with eqn (5.2). Nevertheless some interesting differences may be pointed out. Even though the platelets are eight-sided they lie on \(\{111\}_m\) which has hexagonal symmetry. They are not regular although their sides are, just as in the case of hexagonal platelets, parallel to \(<123>_m\) (viz 1 to 6 in Figure 5.1). The notable difference is that the sides of a given platelet have two directions from each of the two sets of \(<123>_m\), i.e. one direction from each set is missing. This gives three possible orientations. Corresponding to each of these there is a form oriented similarly but its alternate long and short sides are short and long sides of the former. This might lead to a wrong impression that there are six different orientations. Figure 5.3a makes clear how there are only three, not six, orientations of 0-I without re-entrant corners. The two different groups shown are crystallographically equivalent. The grouping and the actual drawing are a matter
of convenience in the discussion of the morphology, but the platelets are observed in the crystals entirely unrelated to and isolated from one another. \( <123> \) directions are denoted by numbers from 1 to 6 at the inner boundaries of the platelet forms. The orientations shown in each group are such that \( (1,6) \), \( (2,4) \), and \( (3,5) \) directions are missing. As remarked earlier, this results in three distinct orientations on a given \( (111) \). These orientations are both established by X-ray analysis and in accordance with microscopic observations. The 0-I platelet shown on the stereographic projection of Figure 2.26 corresponds to the lower left of Figure 5.3a, i.e. its sides are \( (1,3,5,6) \), with \( (2,4) \) missing. Another way of looking at these is that, given six \( <123> \) -directions from which four are to be chosen, there are but three ways in which an octagonal platelet without re-entrant corners can be formed. In addition to these features it is interesting to note that the geometry of platelets in one group is such that they cannot be interchanged or made to coincide by pure translation. However, in each group a given platelet can be made to occupy any of the remaining two orientations by a pure rotation of 60° in one sense or the other. The platelets in one group can be made to coincide with those in the other by a reflection on \( <112> \) (and, if necessary, a 120° rotation).

From the point of view of the crystal structure of the matrix the respective numbers of orientations of H-I and O-I are different, viz two of the former but three of the latter, on a given \( (111) \).
Fig 5.3 (b) Showing an octagonal platelet form
(see also Fig 5.3 (a))
For the precipitate structure, however, there are but two orientation in either case. The orientational relationship

\[ <123>_m \parallel <110>_p \] (see eqn 5.2)

shows that these two are obtained by rotations of \( \pm \cos^{-1} \left( \frac{5}{\sqrt{28}} \right) = \pm 19^0 0.6' \), which is the angle between \(<123>\) and \(<110>\), from \(<110>_m\).

Looking at \(<110>_p\) directions in Figures 5.2 and 5.3a one sees that this is indeed so.

Hexagonal platelets, being regular, will be similar and the size of a platelet will depend upon how long a time it has had to grow. The growth and shape of an octagonal platelet will depend upon other parameters also. An interesting, albeit not-of-much-use, calculation regarding the shape (in other words, the ratio of sides \(a/b\)) of a platelet may be made on the lines of Curie’s famous calculation regarding the shape of a crystal. In Figure 5.3b let \(\gamma_a\) and \(\gamma_b\) be the 'line energies' of the boundaries \(a\) and \(b\). We assume that after the platelet has grown fully, its area remains constant but the shape adjusts till the total line energy

\[ E = 4 \left( a\gamma_a + b\gamma_b \right) \] (5.3)

is a minimum. The area is given by

\[ A = (a^2 + ab + b^2) \sin \Delta + \sqrt{3} ab \] (5.4)
where

\[ \Delta = \alpha - (\pi/3) = 2\pi/3 - (\pi - \alpha) \]

\[ = 2\pi/3 - \cos^{-1} (13/14) \]

so that \( \sin \Delta = 4\sqrt{3}/7 \)

Minimizing \( E \), we have

\[ \delta E = \gamma_a \delta a + \gamma_b \delta b = 0 \]

or

\[ \delta b = ( -\gamma_a/\gamma_b ) \delta a \] (5.5)

Since the area must remain constant, \( \delta A = 0 \) so that we have, using eqn 5.5,

\[ (\gamma_a/\gamma_b) = (8a + 11b)/(11a + 8b) \] (5.6)

A measurement of the sides of an octagonal platelet should give \((\gamma_a/\gamma_b)\).

This calculation is given here simply to indicate a possible way in which an octagonal platelet could after growth alter its shape. In the context of interfaces the concept of line energy is not a very useful one.

5.3.3 **Decagonal Platelets D** (Figures 2.23-2.25)

Looking at matrix structure, there are on a given \((111)\)_m six orientations of decagonal platelets. The sides of any of them are parallel to a set of five of the six \(<123>_m\) -directions.
Fig. 5.4 Six possible orientations of a decagonal platelet parallel to $(111)_m$. The lines outside the platelets are parallel to $(110)_m$. 
That is, in each, one \( <123> \) is missing. The arguments given above in §§5.3.1-5.3.2 explain these observations also. Figure 5.4 shows these six orientations, grouped in two groups. \( <110> \) directions are not shown here in order to avoid confusion. Again, from the point of view of platelet structure, the two groups correspond to two orientations exactly as in H-I and O-I. One can again look at this as follows: Given six \( <123> \), there are only six ways in which a decagonal platelet may be formed. Platelet geometry is similar to that of O-I, i.e. the two groups cannot be made to coincide by pure translation and/or rotation. A reflection is required.*

5.3.4 Rhombi and Other modified Forms

A number of parallelogram-shaped and rhombic platelets and others which are modified forms of them in several different orientations are seen on a given \((111)\). Three different forms \((\text{Rh}, P, \text{Rh}')\) are shown in Figure 2.27 though they are not shown on the stereographic projection of Figure 2.26. Their sides, as established by back-reflection Laue analysis, are parallel to any two \( <123> \). No drawing corresponding to Figures 5.2-5.4 has been included herein, but it will be straightforward to imagine from these figures the rhombic platelet in its multitude of forms (cf Figure 2.27).

*In order to correspond with Figures 5.2 and 5.3a so far as platelet structure is concerned, the groups in Figure 5.4 should be interchanged.
Fig 5.5 Showing a $\text{BaCl}_2$-platelet and interfaces I, II and III generated with the $\text{NaCl}$-matrix
There is an interesting and surprising difference from H-I, O-I and D, viz the existence of re-entrant corners (Figures 2.27c,d). The extra side is always towards the acute corner of the platelets. This too can be in any one of the several different possibilities (which can be worked out easily on the basis of the discussion in §§ 5.3.1-5.3.3). The interpretation of this phenomenon must involve concepts of 'line' and 'corner' energies.

5.4 Coherent Heterocrystalline Interfaces as Energy Minima

We now proceed to discuss the structure and energy of (111)-interfaces (and also others) on the basis of the idealized morphology of the various forms of platelets discussed in the last section in terms of orientational relationships. As pointed out in § 4.7 the generation of heterocrystalline interfaces between the terminating planes of the platelets and the adjacent planes of the matrix may be looked upon as 'internal epitaxy'. These interfaces will now be examined in the light of current theories developed by van der Merwe, Fletcher and others for epitaxial interfaces (§ 4.6). One aspect of the interfaces under study that is different is that a given platelet has more than one interface. This is not so in epitaxy where one single interface is formed. For instance, the number of interfaces generated by the formation of a hexagonal platelet is eight. For convenience, they may be grouped and designated as: Interface I, Interface II and Interface III as shown in Figure 5.5. They are formed respectively between
(I) the lower terminating \{111\}_p-plane and the \{111\}_m-plane below it,

(II) the upper terminating \{111\}_p-plane and the \{111\}_m-plane above it, and

(III) the terminating \{112\}_p-prism planes and the adjacent \{145\}_m-planes.

In the third column of Table 5.1 the orientational relationships of all interfaces are summarized. The terminating cation and anion \{111\}-layers in the matrix and precipitate structures are also shown for interfaces I and II, but it is clear that I and II are interchangeable. Each platelet must have one of one type and the other of the other type. In principle there is nothing to prevent different platelets in a given crystal from having lower (or upper) m-layer made of differently charged ions. In other words, side by side with a platelet of the description given in Table 5.1 there could be another for which interface I is \{111\}_m^{+} || \{111\}_p^{-} and II is \{111\}_p^{++} || \{111\}_m^{-}. If there is any feature to enable distinction we have been unable to identify it.
### Table 5.1

Showing the number and kind of interfaces between m and p

<table>
<thead>
<tr>
<th>Interface</th>
<th>Platelets</th>
<th>Orientational Relationships</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

In the case of interfaces III both planes contain both cations and anions.

When enquiring into the question of energies of these interfaces contributions due to misfit ($E_m$) and due to elastic distortion ($E_e$) have to be considered to start with. Since both structures are ionic it may be anticipated that there will be an electrostatic contribution ($E_{es}$) by charges which have not been fully compensated across the interfaces. Thus the total interfacial energy is given by

$$E = E_m + E_e + E_{es}$$  \hspace{1cm} (5.7)  

all quantities being referred to unit area. Denoting the total energies of the three interfaces by $E(I)$ etc, we see immediately
Fig 5.6 Showing (a) \{11\bar{1}\}_m (b) \{11\bar{1}\}_p
Fig 5.6 Showing superposition of atomic positions of \( \{111\}_m \) and \( \{111\}_p \) (See also Fig 5.5(a,b))

(c) angle of rotation \( \phi = 0, \) \( <110>_m \parallel <110>_p \)

(d) \( \cos \phi = 5/\sqrt{28}, \) \( <123>_m \parallel <110>_p \)
that \( E(\text{I}) \) and \( E(\text{II}) \) are equal and that either is less than \( E(\text{III}) \). This is because interfaces I and II are formed between planes which are simpler than those between which interface III is formed. From the high surface/volume ratio of the platelets we can also conclude that \( E(\text{III}) \) is likely to be much greater than \( E(\text{I, II}) \). In § 5.3 it was asserted that interfaces I and II are coherent. We now expect interface III to be incoherent.

The lattice distance relationship (5.1) corresponds to a lattice distance ratio of

\[
\frac{b}{a} = \frac{|<110>_p|}{|<123>_m|} = 1/2
\]  \hspace{1cm} (5.8)

We see in Figure 4.6 that, according to Fletcher, there is a cusped minimum at this value. We look upon the matrix here as the 'substrate' and the precipitate platelet as the 'overgrowth'. This description is clearly compatible with the actual physical situation, since it is the overgrowth/precipitate atoms which condense on/in the substrate/matrix.

For this purpose let us look at the superposition of planes \{111\}_m and \{111\}_p (Figure 5.6(a,b)), drawn to scale as to the values of \( a \) and \( b \), as a function of azimuthal rotation \( \phi \) about the common \( <111> \)-direction. Figure 5.6(c) shows the superposition without any rotation \( (\phi = 0) \); crystallographic directions of the one are parallel to those of the other. In particular, \( <110>_p \parallel <110>_m \) in this figure. If the superposition is such that, as in
this figure, a p-atom (Ba++, represented by a dot) sits exactly in a close-packed position in the middle of three m-atoms (Cl-, represented by a circle), then close-packing is not preserved to any great extent.

The problem is similar to the one considered in detail recently by Bollmann (1970) and it will be useful to mention in brief Bollmann's elegant geometrical theory. Bollmann considers crystal interfaces generated by joining together two identical crystals of different but known orientations. Before joining, parallel plane (or, in general, parallel curved) cuts are made in each. A total of five parameters are required: three for prescribing relative crystal orientations and two for defining the boundary plane. This way of analyzing the problem is almost intractable even if atomic relaxations are not allowed. Also, a separate theory would be required for each differently oriented interface. Bollmann therefore has another approach whereby he looks for some basic principle that might be thought to operate no matter what orientations are involved. He states this as the principle of 'conservation of crystal structure': "Crystals tend to match at the boundary". Conversely, a boundary tends to pass through regions of good match. Atomic relaxation is permitted at this stage, and we see that regions of good match will tend to extend while those of bad match will tend to contract into dislocations. When regions of mismatch are rather widespread (i.e. in the case of 'high angle boundaries') the crystals might like to preserve
at least a small part of the original structure. In other words, and more exactly, there might be built a common superlattice that is a coincidence site lattice (CSL). For the purpose of predicting primary dislocation networks which comprise the interface concerned, Bollmann has defined the 'O-lattice'. It is the lattice of coincident points which have the same internal co-ordinates in the two structures. This O-lattice involves the entire continuous space of the two structures as well as the discrete lattice points. Clearly the points of CSL are members of the O-lattice. Bollmann has given (loc cit) a mathematical procedure for calculating the O-lattice in general. The interface then is an appropriate section through the O-lattice. 'Good matching' is obtained around the points of the O-lattice while for obtaining regions of 'bad matching' we construct Wigner-Seitz cell walls.

The Bollmann theory in its present form is applicable to interfaces formed between identical crystals. The problem at hand in the present work is even more complicated. It is for this reason that we adopt a procedure whereby a reasonably correct structure of the interface can be predicted, relying mainly on any conservation principles which may be operative. In a manner similar to Bollmann's we assert that our coherent interface is built in such a way as to conserve close-packing across it. Returning to Figure 5.6c we see that within three or four interatomic distances m-atoms occupy almost labile positions. A simple calculation shows that

\[
| \langle 112 \rangle_p | = \sqrt{3} \quad | \langle 110 \rangle_p | = 1.732 \quad | \langle 110 \rangle_p |
\]
whereas the corresponding distance in the chlorine-lattice is

$$\frac{8}{\sqrt{21}} = 1.748 \quad <110>_p$$

using the relation (5.8). The difference of about 0.5% makes the corresponding atoms almost coincident, and it is not surprising that the system avoids such an orientational relationship.

The matter can be looked at from another point of view. Figure 5.6c is essentially a Moiré pattern. Looking at it at a glancing angle along a $<110>$-direction we see that 'bright' strip-like areas are too few. In Moiré terminology we could say that MS-lines ("minimum strain") are too few. What we really mean by either description is that the 'matching' is poor.

When the p- and m-planes are rotated with respect to each other about the common $<111>$-direction in the range $\phi = 0^\circ - 60^\circ$ a continuous series of interfaces is generated. Their energies can be examined as a function of $\phi$. After rotation in each case atomic relaxations will be allowed, and clearly they will in each case reduce the energy somewhat. The most interesting orientations are when $\phi = \cos^{-1}(5/\sqrt{28}) = 19.07^\circ$ (Figure 5.6d) and $\phi = \cos^{-1}(4/\sqrt{28}) = 40.05^\circ$. The two are geometrically and physically identical; in either orientation, $<110>_p | | <123>_m$. Figure 5.6d (as also a simple calculation based on eqn 5.8) shows that along $<110>_p$ every alternate Ba$^{++}$ is in a close-packed position without relaxation. Relaxation is required for the remaining 75\%
Fig 5.6(e) Energy cusps corresponding to interfaces I and II.
of Ba\textsuperscript{++}-ions and it leads every one of them to a close-packed position nearby. The relaxation itself being a function of $\phi$, the system will have that orientational relationship which reduces the relaxation required and also brings ions to better close-packed positions. If Figures 5.6a and b are traced on tracing paper superposed and rotated with respect to each other it can be seen, by looking at a glancing angle and by using the 'MS-elements' criterion, that these two orientations are likely to be energy minima. The exact calculations are obviously very difficult and have not been attempted here. Figure 5.6e shows a schematic graph of $E(\phi)$. The dashed lines represent the energies of relaxed interfaces. It should be noticed that the difference between the full and dashed curves is the least at energy cusps. Thus the observed orientational relationship (eqn 5.2) is seen to be fully compatible with the 'geometrical minimum'. We guess that this would also turn out to be a 'physical minimum'.

The detailed close-packed structure is proposed in the following section.

5.5 Close-packed Stacking of Layers of Interfaces I and II

5.5.1 An extension of this application of the principle of conservation of close-packing is the further assertion that close-packing be preserved not only at the interface but also across it on both sides. The stacking sequences of NaCl and BaCl\textsubscript{2} may be written as
where \((a,b,c)\) and \((A,B,C)\) denote \(Na^+\) and \(Ba^{++}\) while the greek letters denote \(Cl^-\), the dash (') referring to \(BaCl_2\). The layers defined by eqn (5.9) are not in parallel orientation with those defined by eqn (5.10). ((It is useful to look at atomic positions projected on \(\{110\}\) or other planes, for then the three laterally different positions are clearly made out. Figure 5.11 shows \(<110>-\) projections of the two sequences.)) Now the platelets of \(BaCl_2\) embedded in \(NaCl\) can be looked upon as being sets of parallel layers of ions. Suppose that a \(BaCl_2\)-stack is introduced, in the correct azimuthal orientation, into an equivalent 'hole' carved out in \(NaCl\). No matter what the initial lateral relation* there was among the layers of the interface, there will after relaxation be a lateral shift in some or all of the ions of the layers forming the interface. As explained in \(\S\) 5.4, in the orientation observed experimentally 75% of the ions of the interface-layer of \(BaCl_2\) will shift to close-packed positions other than the original type. For the sake of a specific description let us assume that the interface-layer of \(NaCl\) remains rigid so that close-packing could be described in terms of it. Essentially, this description is the

*That is, in terms of \(A,B,C\)-type positions.
converse of what actually must happen when precipitation takes place, but it is more convenient than one involving the details of the process of precipitation.

In order that the description thus taken in hand satisfies all criteria of close-packing and avoids juxtapositioning labile symbols after the sequence of eqn 5.9 we shall write the stacking sequence of BaCl₂ rather as

\[ . \ C \ a' \ y' \ A \ b' \ a' \ B \ y' \ b' \ . \ ] \quad (5.10a)

it being kept in mind that only 25% ions of the first layer of this (viz C) are strictly in C-positions. As soon as, at this stage, relaxation occurs 75% ions of this layer will take up A-positions and it would be necessary to rebuild the further stacking in terms of this majority of ions, viz

\[ . \ A \ b' \ a' \ B \ y' \ b' \ C \ a' \ y' \ . \ ] \quad (5.11)

Although this looks identical to the sequence (5.10) there is a conceptual difference and it is the following: Each of the sequences (5.9) and (5.10) has a six-fold degeneracy and one could start with any one of the six expressions for NaCl and juxtapose with it any one of the six expressions for BaCl₂. However, the requirement of close-packing would reduce the degeneracy. Since the interface-layer of NaCl is being held rigid we start with the particular
Fig 5.7  Showing stacking of \{111\}_m and \{111\}_p
sequence of eqn (5.9) and always keep to it. A moment's reflection will show that, not considering relaxation, only the sequence of eqn (5.10a) can be juxtaposed between two sequences like eqn (5.9). If we then allow relaxation most ions of what was called C-layer take up A-positions. Of the two possible sequences starting with A, viz Ay'a' ... and Aβ'α'... we choose the latter since 25% Ba++ of the A-layer are in their original, i.e. C, positions. The stacking sequence for the entire system inclusive of the interfaces would then look like

\[ ... a \gamma b \alpha c \beta | (\frac{A}{C}) \beta'\alpha' B \gamma'\beta' C \alpha' (\frac{\beta'}{\gamma'}) | a \gamma b \alpha c \beta ... \]

+ matrix +I+ platelet +II+ matrix + (5.12)

wherein the lateral shift of 75% of Cl⁻ in γ'-positions into β'-positions has been taken care of. This last point is most easily seen by approaching the platelet from the side of interface II rather than interface I. In any case the complete sequence of (5.12) is obtained. This is shown schematically in Figure 5.7.

5.5.2 We are now in a position to discuss the detailed close-packed structure of interfaces I and II. For interface I it is obtained directly from Figure 5.6d after allowing relaxation and representing ions by large circles drawn to scale (as to ion diameters). The structure for interface II is obtained by imagining the rotation \( \phi = \cos^{-1}(4/\sqrt{28}) \) to have been performed in Figure 5.6 and, further, relaxing atoms etc. The structures obtained in this way are depicted in Figures 5.8a and b respectively. In each case
Fig 5.8 Showing structures of (a) $\beta/(A\gamma^C)$ - interface, (b) $(B\gamma^f)/a$ - interface

- $\text{Cl}^-$
- $\text{Ba}^{++}$
- $\text{Na}^+$
it is the matrix ions (Cl⁻ and Na⁺ respectively) which are held fixed and the precipitate ions (Ba²⁺ and Cl⁻ respectively) which are allowed to relax.

Returning to Figure 5.6d we see that a rather simple two-dimensional superlattice is formed for \( \phi = \cos^{-1} \left( \frac{5}{\sqrt{28}} \right) \) (and correspondingly for \( \phi = \cos^{-1} \left( \frac{4}{\sqrt{28}} \right) \)). The unit cell shown, KLMN, conforms to the 3-fold symmetry.* The Ba²⁺-ions at K,L,M,N are already in close-packed positions. (They correspond to one of four Ba²⁺-ions in the unit cell, i.e. 25%). The other ions need to be relaxed along three \( \langle 112 \rangle_m \)-directions before they occupy close-packed positions. The resulting superlattice can still be described by the same unit cell, KLMN, because the relaxations themselves conform to its symmetry. This superlattice of Figure 5.8a (or b) has the symmetry of the plane group p\( \overline{3} \). Figure 5.8a for interface I is drawn with a precipitate ion (Ba²⁺) at the centre whereas Figure 5.8b for interface II is drawn with a matrix ion (Na⁺) at the centre, but they could be drawn differently.**

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* The original 6-fold symmetry (p\( \overline{6} \)mm) of both \{111\}_m or \{111\}_p is now reduced to 3-fold.

** The C- and \( \gamma' \)-positions labelled in Figures 5.8a and 5.8b respectively in the platelet layer are the unrelaxed positions of ions whereas those not labelled in the same layer are the A- and \( \beta' \)-positions occupied by ions after the relaxation following the stacking sequence of equation (5.12).
Fig 5.9 Key to Fig 5.10
Fig 5.10  Showing structure of interface III

○ Na⁺,  ○ Ba²⁺,  ○ Cl⁻
Fig 5.11 Showing positions of ions projected on (a) (110)\textsubscript{m} (b) (1\overline{1}0)\textsubscript{p} (c) (12\overline{3})\textsubscript{m}

○ Na\textsuperscript{+}, ○ Ba\textsuperscript{++}, ○ Cl\textsuperscript{−},
What is important is the p3-symmetry.*

Thus the actual interface is obtained by a re-positioning of some ions in the terminating \(\{111\}^{++}_p\) and \(\{111\}^+_-\) layers of a platelet. Clearly, within the platelet, i.e. far from either terminating layer, the normal p6mm-symmetry must be obtained to make the bulk of the platelet a perfect BaCl₂-structure. We expect the transition from p3- to p6mm-symmetry to be effected within a few layers on both sides. Further, we also expect distortions on the matrix-side of each interface in a similar way, but they will be such as to preserve close packing at the interfaces.

5.6 Structure of Interface III

Using eqn (5.2) it is easily seen that the orientational relationship across the prism faces of a platelet is

\[
\{145\}_{\text{NaCl}} \parallel \{112\}_{\text{BaCl}_2}
\]

\[
<111>_{\text{NaCl}} \parallel <111>_{\text{BaCl}_2}
\]

(5.13)

It should be a rather complicated structure. The best way to visualize the structure is to view it along the direction \([\overline{1}23]_m\) \(\parallel [\overline{1}10]_p\). Figure 5.9 shows the orientational relationship (5.13) above and the direction of viewing; it also acts as a key to Figure 5.10 which shows the structure of the incoherent

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*The symbols 'p' and 'm' of the notation for plane groups here should not be confused with the letters p and m used to abbreviate 'precipitate' and 'matrix'. The context makes things clear.
interface III obtained by embedding Figure 5.11b in 5.11c. PQRS is a section of a platelet showing the positions of the ions of the precipitate in relation to those of the ions of the matrix.

The fact that interfaces III are incoherent helps us see that the precipitates exist as platelets rather than bodies with the three dimensions comparable in extent.

5.7 Electrostatic Energy of the Interfaces

As the interfaces are formed between two ionic crystal structures (NaCl and BaCl$_2$) it is necessary to look into the question of the possible excess charge (or otherwise) on them. A simple calculation shows that the (A$^\prime$)- and (B$^\prime$)-layers have excess charges due to the aliovalence of Ba$^{++}$. The excess, i.e. uncompensated, charge densities on them are $(+e/2\sqrt{3}b_0^2)$ and $-(e/2\sqrt{3}b_0^2)$ respectively where $b_0 = 7.34 \, \text{Å}$ (lattice constant of BaCl$_2$) and $e$ is the electronic charge. An interface may be expected to build up so as to leave suitable vacancies within itself such that there is no excess charge. All attempts to generate suitable vacancies or to replace some Ba$^{++}$ by Na$^+$, and vice versa, for this purpose have proved fruitless. There does not appear to be any simple way of neutralizing the excess charge density on either of the interfaces, although as a whole the platelet is neutral. The local field of the excess charge density and the consequent electrostatic energy, $E_{es}$, must therefore be considered. $E_{es}$ is then one more contribution to the total interface energy.
Considering the interface as a sheet of charge with areal density $\sigma$ (coul m$^{-2}$) in a dielectric of constant $K$, we get the energy density (j m$^{-3}$) as

$$U = \frac{1}{2} K \varepsilon_o E^2$$

$\varepsilon_o$ being the permittivity of free space. The effect of this charge sheet is felt, at the most, for one interplanar distance, say, $h$. The energy (j m$^{-2}$) in the dielectric is then

$$E_{es} = \frac{1}{2} K \varepsilon_o E^2 h$$

$$E = \sigma/2 \varepsilon_o = (e/4\sqrt{3} \varepsilon_o b_o^2)$$

Hence

$$E_{es} = \frac{1}{2} K \varepsilon_o (e/4\sqrt{3} \varepsilon_o b_o^2)^2 h$$

$$= \frac{1}{96} (Khe^2/\varepsilon_o b_o^4)$$

(5.14)

Using the values $K = 5.6$ (for NaCl), $b_o = 7.34 \times 10^{-10}$ m (for BaCl$_2$), $h = 1.6 \times 10^{-10}$ m, $\varepsilon_o = 8.8 \times 10^{-7}$ coul m$^{-1}$, we have

$$E_{es} = 10^{-1} \text{ j m}^{-2} \text{ or } 100 \text{ erg cm}^{-2}$$

(5.15)

In the next section we shall compare this value with the elastic contribution.

5.8 Elastic Contribution

Van der Merwe (1964) has calculated that the elastic energy of an interface is
\[ E_0 = G\left(\frac{1-\sigma}{1-2\sigma}\right)h \ (\Sigma \varepsilon)^2 \]  

(5.16)

where \( G \) = shear modulus of the epitaxial layer, \( \sigma \) = its Poisson ratio, \( h \) = its thickness, \( \Sigma \varepsilon \) = the total strain. The situation for which this expression was derived is not the same as the present one. However, it could be used to get an idea, even if very rough, of the order of magnitude of quantities. The unit cell of the interface of Figure 5.6d may be, for the purpose here, considered to be distorted when relaxations occur as shown in Figure 5.8. The total shear strain is easily calculated to be

\[ (\Sigma \varepsilon) = (8/5/21) \]

considering the interface (of suitable shape, i.e., as a rhombus similar to the unit cell) as a distorted plate. Using the values \( G = 10^{11} \text{erg cm}^{-2} \), \( \sigma = 0.2 \), \( h = 1.6 \times 10^{-8} \text{ cm} \) and \( \Sigma \varepsilon \) as given above, we have

\[ E_e \approx 120 \text{ erg cm}^{-2} \]  

(5.17)

The calculations leading to the values of \( E_\text{es} \) and \( E_e \) given by equations (5.15) and (5.17) are admittedly extremely crude. But perhaps they do give a rough comparative idea of the two different contributions. At the least we could conclude that the electrostatic contribution is of the same order of magnitude as the elastic one. A survey of literature available shows that this electrostatic effect is being proposed for the first time.
5.9 **Equivalence of Interfaces I and II**

It was stated in §5.5.2 that the symmetry of I and II is the same. It is possible to look at the differences from the point of view of the total energy. Ions of the same sign of charge should tend to keep away from one another whether within a structure or across an interface. Consider interface II. From the point of view of BaCl₂-structure the terminating layer should be γ' whereas the majority of ions at the interface are in a β'-position. This implies a slightly greater energy than in I where the majority of Ba⁺⁺ are in the correct A-position. However, in II the nearest negative NaCl-layer is γ rather than α or β. On the other hand, in I the nearest negative NaCl-layer is β, not α or γ, against β'. This would imply a slightly greater energy than in II. We believe that the two effects would compensate each other exactly and that the energies of I and II would be exactly the same. There is in fact no reason for there to be any asymmetry in the energetics of interfaces which are to all purposes identical.

5.10 **NaCl-BaCl₂ as a Transparent Analogue of Al-Cu Alloys**

5.10.1 Precipitation of second phase particles and the control on their size and dispersion in a solid matrix is the basis of the technologically important process of age-hardening. The major portion of the increased strength of alloys like steels, Al-Cu, Al-Cu-Mg, etc arises from such processes. The fundamental
mechanisms occurring have recently been reviewed exhaustively by Kelly and Nicholson (1963) and by Brown and Ham (1971). There is little doubt that essentially the cause of strengthening is the interaction of dislocations with precipitates. But the details depend upon a number of other parameters: Are the precipitate particles coherent? Are they deformable? Are they stronger than the matrix? What are their shapes? What is their dispersion? and so on. For the sake of theoretical simplicity, spherical particles are usually assumed. Also it is assumed that the average "wavelength" of their distribution is greater than their average diameters. Consequently, alloys which do not satisfy those and such discriptions cannot be adequately treated. Al-Cu alloys belong to this class.

There are several characteristics of the Al-Cu system (and, perhaps, of other systems) which are seen in the NaCl-BaCl$_2$ system under study. Some important points of this similarity are given below.

(a) The shape of particles in Al-Cu is far from spherical or even approximately equiaxed. They are in fact rods and thin discs. The GP zones are nearly pure Cu-layers parallel to \{100\}-planes and are only one atom thick; the \(\theta\)"-phase is a disc with an overall composition CuAl$_2$ and is ordered (one Cu-layer alternated with three Al-layers, parallel to \{100\}-planes). The polygonal precipitates under discussion here are also thin platelets with a definite composition (BaCl$_2$).

(b) The average distance between particles (GP zones or \(\theta\)") is comparable to the average particle diameter. This is true in the NaCl-BaCl$_2$ system also.
(c) The effect of (b) above in Al-Cu is that the yield stress is insufficient to enable dislocations to expand between obstacles. It will be useful to investigate if this is also so in NaCl-BaCl$_2$.

(d) The fact (a) above implies that the precipitates in Al-Cu are coherent. We have shown in the present work that the precipitates in NaCl-BaCl$_2$ are coherent. In the case of such precipitates the resistance to shear is governed by the interaction between a moving dislocation and the stress field around a precipitate at rather short distances. In NaCl-BaCl$_2$ such a short-distance interaction will necessarily involve the electrostatic charge at the interface.

(e) The deformation in Al-Cu occurs mainly by primary slip and the zones are sheared with the matrix. Further planned work on the NaCl-BaCl$_2$ system should show whether this is so in it. If so, it may be possible to extend detailed mechanisms in one system to the other. If, however, the slip planes of p and m are not parallel, as seems to be the case for NaCl-BaCl$_2$, strength is increased (other things remaining identical) because of the sessile jogs created at the interface.

(f) Finally, we would like to stress the role of interfacial energy in determining the microstructure and hence mechanical properties. A trace of a third element (such as Cd in Al-Cu-Cd) might alter the interfacial energy in just the right way. It is planned to attempt to do so for the NaCl-BaCl$_2$ system.
5.10.2 It is thus seen that the NaCl-BaCl₂ system affords a close analogue to Al-Cu. As both of the salts are transparent it affords the obvious facility of using an optical rather than electron microscope. The processes which one sees while experimenting with thin foils in the electron microscope may not exactly be the same in the bulk. For example, the electron microscope shows dislocations avoiding precipitates in Al-Cu by cross-slip to the surface. This would not happen in bulk material. It is therefore quite possible that by exploiting the analogous behaviour of NaCl-BaCl₂ one can gain some insight into the processes taking place in Al-Cu.

We thus call NaCl-BaCl₂ "transparent duralumin" in the same spirit that Nye and Crowan called AgCl "transparent metal".

5.11 Summary

The more important conclusions of the analysis are summarized below.

(1) The idealized morphology attributable obviously to the BaCl₂-platelets in the cubic phase (hexagons, octagons, decagons, rhombi and modified forms of these) is consistent with the following orientational relationships:

\[ \{111\}_{\text{NaCl}} \parallel \{111\}_{\text{BaCl}_2} \]

(a)

\[ \langle 123 \rangle_{\text{NaCl}} \parallel \langle 110 \rangle_{\text{BaCl}_2} \]  

\[ (5.2) \]
(2) The relationships (a) above lead to the formation of platelet-matrix heterocrystalline interfaces which are coherent, whereas (b) lead to those which are incoherent. The former are parallel to the platelet plane and the latter to prism faces of platelets.

(3) From the point of view of geometrical structure the coherent interfaces are shown to be cusped energy minima. There is a simple integral relation between corresponding interatomic distances:

$$b/a = (|<110>_{\text{BaCl}_2}|)/(|<123>_{\text{NaCl}}|) = 1/2$$  \hspace{1cm} (5.8)

This supports the conclusions of Fletcher (although his work related to epitaxy only). To this extent we have named the present phenomenon 'internal epitaxy'.

(4) The structure of the coherent interfaces has been proposed in detail. They are shown to be two-dimensional superlattices with a plane group symmetry p3. The basis for this proposal is the 'principle of conservation of close-packing across them'.

(5) Referring to close-packed positions in the matrix of NaCl the total stacking sequence is written down as
... a γ b α c β | (A) B γ' β' C α' (B') | a γ b α c β ...

+ matrix +I+ platelet +II+ matrix → (5.12)

This is consistent with both electrostatic bonding and close-packing.

(6) The structure of incoherent interfaces cannot be written down in this way. But it has been illustrated suitably. It is further believed that interfacial dislocations are not formed.

(7) The coherent interfaces seem to be electrostatically charged, positively and negatively at the two large faces respectively, in a given platelet though as a whole a platelet is neutral. The total energy E of a surface is therefore given by

\[ E = E_m + E_e + E_{es} \]  

(5.7)

where we have added the last term for the first time. The misfit energy \( E_m \) of coherent interfaces is expected to be negligible.

(8) A crude but useful calculation gives the following values for the coherent interfaces:

\[ E_e \sim 120 \text{ erg cm}^{-2} \]  

(5.17)

\[ E_{es} \sim 100 \text{ erg cm}^{-2} \]  

(5.15)

Thus the electrostatic contribution \( E_{es} \) is of the same order of magnitude as the elastic contribution \( E_e \).
(9) This system, viz NaCl-BaCl₂, that is a transparent analogue to technologically important aluminium-copper alloys deserves further study as to the influence of the shape of precipitates and of the interfacial energy on mechanical properties of the matrix.