11.1 Introduction:

Burgers (1940) and Bragg (1940) have shown that low-angle tilt boundaries could be formed by arrays of edge dislocations. The simple example, that of a small-angle tilt boundary, is shown in Fig. 90. Such an arrangement of edge dislocations spaced a distance \( h \) apart, and each with a Burgers vector, \( b \), defines a grain boundary separating two regions of the crystal that differ in orientation by an angle

\[
\theta = \tan^{-1} \left( \frac{b}{h} \right) \tag{11.1}
\]

This formula is valid only for small angles of rotation. However, for large angles of rotation we have

\[
\frac{b}{h} = 2 \sin \left( \frac{\theta}{2} \right) \tag{11.2}
\]

Analysis of grain boundaries, with large disorientation angles is more complicated, since in this case the dislocations are so close to each other that their individual particularities are obscured. Consequently, one must begin the investigations on boundaries with small disorientation angles, since the theory and the experiments relating to such a case can then only be interpreted much more precisely.
The knowledge of the structure and properties of boundaries with small angles will in turn facilitate the solution of more complex problems concerning grain boundaries with large angles. In fact, the discovery of the phenomenon of polygonization and the study of the structure and properties of sub-boundaries helped considerably to widen our concept of intercrystalline boundaries.

Relationships (11.1) and (11.2) give a physical meaning to the dependence of the structure and properties of the boundary on the disorientation angle of grains in a dislocation model. It turns out that the dislocation density depends on the disorientation angle of grains. This can be checked experimentally.

Read and Shockley (1950) predicted certain physical properties such as grain boundary energy on the basis of the assumed dislocation model. Read (1953) proposed a general mathematical formula for the model of grain boundaries. Using this formula, one can construct all the possible types of boundaries composed of different types of dislocations. Using this formula, Amelinckx (1957) has investigated the geometry of dislocation nets and fold boundaries for different crystallographic structures. The structure and properties of grain boundaries were studied in detail by Amelinckx and Dekeyser (1959).
The first investigations concerning the etching of intergranular boundaries on very pure aluminium were apparently made by Lacombe and Yannaquis (1947). They also established qualitatively that not all the grain boundaries are etched at the same rate, the etching rate increases with the difference in the orientation of two neighbouring grains.

The experiments with samples whose thickness was that of the grain are particularly convincing. Under these conditions the distribution of the contours of etching nets on both the sides of the sample turns out to be the same. The fact that the net of etch figures is the same on both sides of the sample shows that they are the result of defects within the sample which extend to the surface.

The confirmation of the correctness of the dislocation model of grain boundaries was done by Vogel and his co-workers (1953, 1955) who thoroughly checked the relationship $\theta = b/h$. The elaborate experiments of Vogel et al (1953) established a one to one relationship between etch pits and dislocations. Vogel et al compared the measured spacing, $h$, of etch pits in a tilt boundary in germanium with the orientation change, $\theta$, across the boundary. The angle $\theta$ was measured by an X-ray method. They showed that the measured spacings are in good agreement with those calculated from the dislocation
model of a grain boundary.

On etching synthetic calcium fluoride cleavages in various etchants, rows of closely packed etch pits were obtained. These rows have a close similarity to those observed in the case of germanium and silicon (Vogel et al, 1953). It was therefore conjectured that these rows may represent low-angle boundaries consisting of arrays of parallel edge dislocations. The decisive evidence in this respect could be had by measuring the orientation of the grains by X-rays. None of the rows of pits in synthetic calcium fluoride was long enough to permit X-ray orientation measurements, so whether they too represent the tilt boundaries could not be checked with X-ray analysis. However, the following considerations enabled the author to determine the nature of the boundary.

Assuming that the boundary represented by the tips of pits, forming rows, is perpendicular to the (111) cleavage plane of synthetic calcium fluoride, one can show from the Frank boundary equation (Frank, 1950) that the boundary model having minimum energy in this case, consists of an array of two kinds of parallel edge dislocations which utilize two of three a/2 [110] Burgers vectors lying in the (111) plane. Thus, if the boundary trace makes an angle $\phi$ with the nearest Burgers vector, then the other two Burgers vectors are
used and the number of dislocations per unit length is given by

\[ n = \left( \frac{\theta}{\sqrt{3}b} \right) \frac{\cos \phi}{\cos \phi} \]

or \[ \theta = \left( \sqrt{3}b \right) \frac{n}{\cos \phi} \] \hspace{1cm} (11.3)

where \( b \) is the magnitude of the Burgers vector and \( \theta \) is the tilt angle of the boundary.

Consider now the intersection of three such tilt boundaries \( A, B \) and \( C \). Then for these intersecting boundaries, we have,

\[ \theta_A = \left( \sqrt{3}b \right) \frac{n_A}{\cos \phi_A} \]

\[ \theta_B = \left( \sqrt{3}b \right) \frac{n_B}{\cos \phi_B} \]

\[ \theta_C = \left( \sqrt{3}b \right) \frac{n_C}{\cos \phi_C} \] \hspace{1cm} (11.4)

The sum of the three angles of tilt boundary must be zero for intersecting boundaries. This means that one boundary, say \( A \), must have the opposite sense of tilt from the other two, so that

\[ \theta_A = \theta_B + \theta_C \] \hspace{1cm} (11.5)
On substituting the values from equation (11.4) in equation (11.5) and simplifying we get,

$$\frac{n_A}{\cos \phi_A} = \frac{n_B}{\cos \phi_B} + \frac{n_C}{\cos \phi_C}$$

Now $\phi$ is the angle between the boundary trace and the nearest Burgers vector. It cannot be greater than 30°, hence the approximate value of $\cos \phi$ is unity. Using this approximation the above equation becomes,

$$n_A = n_B + n_C \ldots (11.6)$$

This equation states that the linear pit density in one boundary is equal to the sum of those in the other two. (This is for $T$-type intersection).

For two intersecting tilt boundaries the relation will be,

$$n_A = n_C \ldots \ldots (11.7)$$

since $n_B = 0$

i.e. for two intersecting boundaries, the linear pit density in one boundary equals that in the other. (This for $L$-type intersection).

Amelinckx (1954) found that this relationship was satisfied in some cases of grain boundary junctions in
sodium chloride, which implied that there is a correspondence between etch pits and dislocations. Pfann and Lovell (1955) made similar measurements in the case of purely rotational boundaries on germanium monocrystals, for which above relationships were also found valid. In the latter work on the dislocational structure of germanium monocrystals by the selective etching method, Pfann and Vogel (1957) also indicated the astonishingly precise way in which above relationships are satisfied in the cases of L and T intersections of boundaries.

Recently, Wagner and Chalmers (1960) measured the relative energies and boundary orientations of simple tilt boundaries in germanium crystals. The measurements were made on columnar tricrystals prepared by the modified Czochralski method. They measured relative grain boundary energies as a function of the angular misorientation $\theta$ between two grains.

In the case of intersecting boundaries consisting of edge dislocations having a single Burgers vector, it can be shown that $n_A = n_B + n_C$ where $n_A$, $n_B$, and $n_C$ are the number of dislocations per unit length in the three branches. Now, the number of dislocations may be counted by the etch pit technique if the etch pits are fully resolved by a microscope. Their spacing, $h$, is
therefore, must be large and hence the tilt $\theta$, should be small. If $\theta$ is large, the spacing between the pits will be small and boundary will be etched, forming an etched groove on the crystal face in which the pits may not be resolved. In this work many such small-angle tilt boundaries are observed on single crystals of synthetic calcium fluoride and are described below.

11.2 Low-angle Tilt Boundaries On (111) Cleavage Faces Of Synthetic Calcium Fluoride:

Fig. 91 (X 550) shows a row of etch pits produced by etching a (111) cleavage surface of synthetic calcium fluoride with 0.15 N nitric acid for about 20 minutes. Because of good resolution the rows of etch pits are clearly visible. From the photograph, the distance between successive pits was calculated and is found to be 1.78 microns. Assuming that the row of pits represents the edge dislocations in a small-angle tilt boundary, the angle of the tilt calculated from the spacing is found to be 5 minutes. In the present investigation the spacing between the pits has been calculated actually by counting the number of pits in 5 cm length at a magnification of about X 1000. Since the tilt is small, the orientation of the triangular pits on the two sides of the boundary appears to be the same. Fig. 92 (X 400) shows a row of etch pits on another etched cleavage face. The author could not verify the tilt as was done by Vogel et al (1953) in germanium, with the help of
X-ray. In order to ascertain whether or not such rows of pits represent the tilt boundaries in synthetic calcium fluoride, the author looked for intersection of such boundaries. Wagner and Chalmers (1960) in germanium, Wernick et al (1958) in antimony and Pandya and Balasubramanian (1963) in antimony have reported that at the junction of three boundaries the relation

\[ n_A = n_B + n_C \]

holds good. Thus fig. 93 (X 350) illustrates an etch pattern wherein three rows of pits are clearly seen meeting at a point. Fig. 94 (X 350) is another good example of the above type.

11.3 Low-angle Tilt Boundaries On Matched Cleavage Faces:

In order to investigate whether these rows represent small-angle tilt boundaries, the matched cleavage faces were etched in 10 per cent sulfamic acid for 25 minutes. Figs. 95(a) and 95(b) (X 250) illustrate the etch patterns on the matched faces. It is surprising to find that exactly similar three intersecting rows of pits are produced even on the matched face. The density of etch pits in each row is counted in both the photographs, and is given in Table No. 11.1.

It may be noted from the observations given in Table No. 11.1 that:

1. The density of pits in any branch on one cleavage face is exactly the same as the density of pits on the corresponding branch on the matched face.
Table No. 11.1

Pit density in pits/micron for intersecting boundaries on matched pairs

<table>
<thead>
<tr>
<th>Particulars</th>
<th>One face</th>
<th>Oppositely matched face</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branch</td>
<td>$n_a$</td>
<td>$n_b$</td>
</tr>
<tr>
<td>No. of Pits/Micron</td>
<td>0.105</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Table No. 11.2

Pit densities in pits/micron of boundary for intersecting boundaries.

<table>
<thead>
<tr>
<th>Junction</th>
<th>$n_a$</th>
<th>$n_b$</th>
<th>$n_c$</th>
<th>$n_b + n_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14</td>
<td>0.056</td>
<td>0.084</td>
<td>0.14</td>
</tr>
<tr>
<td>B</td>
<td>0.11</td>
<td>0.084</td>
<td>0.028</td>
<td>0.11</td>
</tr>
<tr>
<td>C</td>
<td>0.085</td>
<td>0.056</td>
<td>0.028</td>
<td>0.084</td>
</tr>
<tr>
<td>D</td>
<td>0.14</td>
<td>0.085</td>
<td>0.055</td>
<td>0.14</td>
</tr>
<tr>
<td>E</td>
<td>0.11</td>
<td>0.055</td>
<td>0.056</td>
<td>0.11</td>
</tr>
<tr>
<td>F</td>
<td>0.15</td>
<td>0.11</td>
<td>0.040</td>
<td>0.15</td>
</tr>
</tbody>
</table>
2. At the junction of the three boundaries, on both the cleavage faces, the relation \( n_A = n_B + n_C \) is satisfied.

Figs. 96(a) and 96(b) (X 350) represent the etch patterns on another pair of matched cleavage faces. These figures establish, beyond doubt, the exact correspondence of intersecting rows of pits on the matched faces.

These observations thus endorse the view that the rows of pits indicate the rows of edge dislocations in the small-angle tilt boundary.

11.4 Low-angle Tilt Boundaries On The Opposite Faces Of A Thin Cleavage Plate:

Having established that the rows of pits represent small-angle tilt boundaries, the question now arises, "how far within the body of the crystal the boundary plane extends"? The author has an answer to offer to this question. This can be found out (1) by photographing the etch patterns on the two sides of a crystal plate and (2) by the device of cleaving out and etching a small block having four cleavage faces, as was done by Patel and Tolansky (1957) for diamond and Patel and Goswami (1962) for calcite.

A thin plate of a crystal of thickness 1.5 mm. was cleaved and etched in 0.15 N nitric acid for 15
minutes. Thus Figs. 97(a) and 97(b) (× 175) represent the etch patterns of the corresponding regions on the two opposite faces of the plate. It is noteworthy that the etch patterns have not only a complete correlation of the tilt boundaries, but in addition, there is nearly one to one correspondence in the number and position of the individual isolated triangular pits which are not on the boundaries, indicating thereby that the dislocation lines run right through the thickness of the plate.

11.5 Etching Of Cleavage Blocks:

The establishment of a close parallelism between the etch patterns on the opposite faces of a cleavage plate brings in its wake another question, viz. "why should there not be some parallelism between the etch patterns on the opposite faces of a block cleaved from the sides?" The answer to this question was furnished by the device of cleaving out and etching small blocks having four cleavage faces.

On etching such a block, a remarkable correlation in the etch patterns on all its four faces is obtained. These patterns are in fact intimately related. The etch patterns on the four cleavage faces of the cleaved out block are shown in Fig. 98 (× 75), in which they are cut and opened out. Figs. 98(a) and 98(c) represent the
etch patterns on the two opposite faces of the cleavage plate 15 mm. thick, while Figs. 98(b) and 98(d) show the etch patterns on opposite faces joining faces in Figs. 98(a) and 98(c). The correlation in the etch patterns on these four faces is remarkable.

Attention is drawn to the following:-

1. There is one to one correspondence in the rows of pits on the two sides of the crystal plate.

2. The row of pits marked A on face 'a' can be traced on face 'b' and appears again on face 'c' where it is marked 'A'. Here it is seen going right through the body of the crystal and then finally reappearing on face 'd'.

3. The density of pits counted in these boundaries on faces 'a', 'b', 'c' and 'd' are as follows:-

<table>
<thead>
<tr>
<th>Face</th>
<th>Density (Pits/Micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.12</td>
</tr>
<tr>
<td>b</td>
<td>0.118</td>
</tr>
<tr>
<td>c</td>
<td>0.12</td>
</tr>
<tr>
<td>d</td>
<td>0.12</td>
</tr>
</tbody>
</table>

4. The density of pits in the branches B and C on face 'a' is the same as on the branches B' and C' on the face 'c'.

5. For junctions P and P' on faces 'a' and 'c' respectively, the relation \( n_A = n_B + n_C \) is satisfied.

These observations indicate that the edge dislocations in the boundary plane go right through the body.
of the crystal and hence the boundaries formed on the
two faces of the plate due to the same tilt between
two blocks give the same density of dislocations in
all the corresponding boundaries.

11.6 Unusual Observations:

During these investigations on one of the clea­
vage faces investigated, a large number of rows of
pits were found intersecting and forming a number of
junctions with three boundaries each. Thus Fig. 99
( X 125) represents eleven rows of pits intersecting
each other forming six junctions of three boundaries
each. This is schematically shown in Fig. 100 wherein
the rows of pits are numbered. It is clearly seen that
many rows are common to two junctions. The number of
pits/micron in each row was counted and is given in
Table No. 11.2.

It is very interesting to find that for a parti­
cular junction the density of pits in one row equals
the sum of the densities in the other two at each jun­
cction, even though many junctions are interlocked with
common rows. Fig. 101 ( X 350) is another good example
of this type. This figure shows nine rows of pits
intersecting each other and forming five junctions of
three boundaries each. Here also the density of pits
in one row equals the sum of the densities in the other
two at each junction.
11.7 Discussion:

From the observations it is quite clear that the rows of pits in the synthetic calcium fluoride single crystals represent the small-angle tilt boundaries which consist of rows of edge dislocations and the pits in the boundaries reveal the dislocation etch pits. Etch pit data for intersecting boundaries also indicates that the etch pits are sites of dislocations.