A Theoretical Investigation of Deformation Mechanisms in Calcite

by

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(1961)

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September, 1964

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Department of Geology and Geophysics, July 25

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Abstract

A theoretical model for the plastic deformation of calcite, based on symmetry arguments and dislocation theory, is presented. Flow mechanisms suggested by the model conflict with those previously determined by Turner. Predictions from the model include translation gliding on \( e_i, r_i, f_j \) and \( m_i \) parallel to \( <1\bar{1}0> \) ( \( i = 1, 2, 3; j = 1, 2, 3, 4 \) ), and twin gliding on \( r_i \) (+) and (-) senses; \( s = 2.065, 0.630 \) respectively parallel to \( <1\bar{1}0> \), and twin gliding on \( f_i \) (-) sense parallel to both \( <1\bar{1}0> \) ( \( s > 2 \) ) and \( <1\bar{1}2> \) ( \( s = 0.630 \) ). The Turner model, on the other hand, predicts translation on \( r_i \) and \( f_i \) parallel to \( <1\bar{1}0> \). No conflict arises for \( e_i \) twinning (+) sense parallel to \( 100 \) ( \( s = 0.695 \) ) in either model.

Reevaluation of previously deformed calcite crystals (including those compressed parallel to \( (11\bar{1}) = (0001) \) ) confirms the theoretical prediction of twin gliding on \( r_i \) (both senses) and \( f_i \). Experimental data interpreted as confirming translation gliding according to the Turner model may be explained by the theoretical model.

Examination of the calcite structure permits the prediction that the dissociation of complete dislocations in the \( [1\bar{1}0] = [2\bar{1}1\bar{0}] \) ( \( b = 4.99A \) ) directions into extended dislocations along the \( [\bar{3}21\bar{2}] \) directions for the \( f_j \) planes and the \( [1\bar{3}21] \) directions for the \( r_i \) planes is both structurally and energetically favorable. As dissociation occurs, the resulting partials move apart leaving behind them a sheet of unsymmetrical stacking fault with the resulting abnormalities being confined to next-nearest neighbors only. Use of this dissociation scheme leads to the development of a dislocation theory of mechanical twinning in calcite. The relative ease of \( e_i \) twinning over the other potential twin systems as well as the polar character of each of the twinning systems can easily be predicted with this theory.

Recent etch figure studies of deformed calcite crystals are summarized and evaluated in light of the theoretical model. Such studies tend to confirm the predictions of the theoretical model.
Acknowledgements

The author would like to express his appreciation to Professor W. F. Brace of the Department of Geology and Geophysics at the Massachusetts Institute of Technology both for circumstances leading to this thesis and for his guidance during its development. Also, the author would like to extend his thanks to Professors E. Orowan and A. Argon in the Department of Mechanical Engineering and to Doctors H. Heard and M. Friedman of the Shell Development Company, Houston, Texas for their willingness to criticize and suggest the many implications of this thesis.

The author is indebted to Mrs. Barbara Bateman for typing part of this manuscript.
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A. Mechanisms of Single Crystal Deformation

1. Introduction

Plastic deformation may occur by either of three processes: slip (translation gliding), twinning (twin gliding), and kinking, shown schematically in Figures 1 through 4.

Slip and twinning are processes representing shear displacements of atoms in a specific plane and direction within this plane. The essential distinction between the two is that twinning is characterized by a specific degree of shear in such a manner that there exists a twin relation, that is, a definite crystallographic relation, between the undeformed and deformed regions whereas slip represents a displacement or gliding of two portions of the crystal with respect to one another, the individual parts retaining their original orientation.

The third mechanism, kinking, is an organized process of slip on many parallel planes resulting from inhomogeneous stress distributions within the crystal. Experimental evidence suggests that kinking results from bending moments induced in the crystal by the grips and perhaps on
Figure 1

Schematic Illustration of Deformation by Translation Gliding
ends unconstrained

ends constrained

undeformed
a smaller scale by internal stress concentrations such as deformation
twins terminating within the crystal.

2. Translation Gliding

Many crystals deform plastically by means of translational slip
during which one part of the crystal moves as a unit across a neighboring
part. Ideally, such a movement consists of a pure translation so that
the crystal (unconstrained) orientations of the different parts remain
coincident.

The line of intersection of the slip surface with the outer sur-
face of the crystal is a slip band. The fact that such bands can be ob-
served implies that such a deformation is inhomogeneous. The thickness
of the undeformed layers, or glide packets, varies with the test condi-
tions but often is in the range of $10^{-3}$ to $10^{-4}$ cm (8)*. The bands, as
a rule, have fine structures and, in such cases, a macroscopic slip surface
consists of a lamella made up of several thin layers of crystal between
which slip has occurred. For example, in aluminum, the spacing between

* Numbers refer to references listed in bibliography.
Table 1

Slip Planes and Slip Directions of the More Common Ductile Materials

<table>
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<th>At High Temperatures</th>
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<td></td>
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<td>Slip Direction</td>
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<tr>
<td>Al</td>
<td>FCC</td>
<td>(111)</td>
<td>[110]</td>
</tr>
<tr>
<td>Cu</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ag</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Au</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>α Fe</td>
<td>BCC</td>
<td>(101)</td>
<td>[111]</td>
</tr>
<tr>
<td>Ta</td>
<td>&quot;</td>
<td>(112)</td>
<td>&quot;</td>
</tr>
<tr>
<td>W</td>
<td>&quot;</td>
<td>(123)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mg</td>
<td>HCP</td>
<td>(0001)</td>
<td>[1120]</td>
</tr>
<tr>
<td>Zn</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cd</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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</table>
the individual bands is about 200 Å and the amount of slip on each band is approximately 2,000 Å. Such a localization of slip implies that the atoms slide past each other by many atomic spacings on the surfaces where the slip takes place.

It is possible for dislocations to have any arbitrary direction and shape in a crystal. However, the presence of preferred growth directions and thermal stresses during solidification, as well as mutual interactions between dislocations will make the dislocations lie on definite crystallographic planes and directions. As a rule, these planes are usually planes of densest packing with large interplanar separation. Similarly, dislocation directions are directions of densest atomic packing within the densely packed plane. Thus in most crystals, slip is on densely packed planes in densely packed directions. However, in some lattices like the BCC metals, dislocations do not find any particular plane more favorable to be on, but the slip direction is invariably the direction of closest packing.

Finally at elevated temperatures, the increased thermal motion enables the dislocations to lie on planes with a less dense packing than
Figure 2

Illustration of Twin Gliding Elements
Figure 3

Schematic Construction of the Contour and Burgers Vector $b$ for a Twinning Dislocation with the Pure Edge Orientation
the ones preferred at lower temperatures. Table 1 below shows the slip planes and associated slip directions of a few important materials and the slip system variation with temperature.

3. Twin Gliding

Plastic deformation by mechanical twinning (Fig. 2) differs from translation gliding in several ways; the main features of which include (8):

a. Sections of the stressed crystal deform into a new orientation which usually is symmetrically related about a rational crystal plane to the undeformed sections of the crystal.

b. Macroscopically, the twinned lamella is generated by a simple shear on the twin plane ($K_1$) in the twinning direction ($\eta_1$). The deformation, in contrast to slip, is homogeneous and is strongly governed by the crystal structure.

c. Microscopically, each atomic plane parallel to $K_1$ slides over the preceding one in the twinning direction a distance fixed by the crystal structure.

The boundary between the twinned regions need not necessarily
be a translation plane nor for that matter, even a lattice plane. If a
twin of the first kind (7) is bounded by a lattice plane, one then speaks
of a coherent twin boundary - a boundary generally representing the least
amount of interfacial energy. The twin boundary need not be confined to
one lattice plane and can pass from one plane to a neighboring one. In
this case, then, the translation plane is said to be bounded by a twinning
dislocation (Figure 3).

In view of the necessary geometrical relationship between the
Burgers vector of this dislocation and the primitive lattice vectors, it
can easily be shown that a twinning dislocation must be a partial dislo-
cation. Such reasoning follows from the observation that the twinning
translation is always smaller than the slip translation.

Finally, if Figure 3 is regarded as referring to a FCC lattice,
the twinning dislocation depicted is in fact a Shockley (8) half dis-
location - i.e., the twinning replaces the cubic stacking by a hexagonal
stacking over a width of the two octahedral planes. Similarly, a twin
in the FCC structure may be regarded as a continuous series of stacking
faults on neighboring lattice planes. Hence it is not surprising that
the generation of a twin on the lattice is directly related to the motion of partial dislocations. These and related observations will play an important role in the formation of a twinning model for calcite (Part III, B).

4. Kinking

During a deformation test, stress concentrations often occur near the grips or near other places. They can give rise to peculiar local formations of slip lines and shapings of the specimen, especially in hexagonal crystals (Zinc, cadmium, magnesium, etc.) where basal glide takes place almost exclusively.

When during or after a bending test of a crystal showing single glide, the temperature being high enough, polygonization may occur, resulting in a decrease of the dislocation density and a redistribution of these dislocations, as indicated in Figure 4 below. The dislocations become aligned in rows perpendicular to the glide planes, which give rise to a special deformational pattern known as kinking. Such unhomogenities have been observed not only in bending tests but also in extension and compression experiments on single crystals (1,2,8,21,24,28).
Kink Formation by Slip on Parallel Crystallographic Planes (K and K' are the kink planes)
There appears to be an analogy between the kinks formed in hexagonal metals and the various types of deformation bands* observed in FCC metals (aluminum, etc.). It is usually found that these result by the mutual hindrance during easy glide (i.e., only one slip system being operative) of the motion of dislocations of opposite sign on neighboring glide planes.

Honeycombe (21) found in deformed aluminum crystals two distinct types of inhomogeneity which were responsible for local reorientations within the crystal lattice. First, narrow bent zones were observed which separated relatively unbent regions of the crystal (kink bands). This mode of deformation was found to give rise to X-ray asterisms. The other type of inhomogeneity comprised bands which were initially deficient in primary slip traced – i.e., traces of the slip system normally expected to function. These bands were approximately parallel to the active slip planes in the early deformation history, and as the deformation proceeded,

* The term deformation band has been utilized in the past to cover all disorientations encountered in both deformed metals and non-metals. As a result considerable confusion exists as to its exact meaning. Following Honeycombe's classification, we shall drop the term and use in its place the terms kink band and band of secondary slip.
the bands became the preferential sites for secondary slip on planes not predicted by the criterion of maximum shear stress. This inhomogeneity is referred to by Honeycombe as "bands of secondary slip". Such bands, although leading to disorientation within the crystal, are primarily free from severe curvatures.

Burgers and Ploos van Amstel (21) have shown that the angular range of asterisms from deformed aluminum crystals is less for a given strain when the crystals deform from the start on two slip systems, than when slip occurs on a single system. Honeycombe's results also indicate this conclusion.

In conclusion, in Honeycombe's experiments, no kink bands were formed in crystals oriented for multiple slip (i.e., 2 or more operative slip systems). Such a result appears reasonable for if another slip plane is available on which the resolved shear stress is similar to that on the primary plane, then the formation of kink bands is unnecessary because the stresses set up as a result of the constraints imposed on the crystal, are reduced by slip on an alternative system.
B. Visual Characteristics of Single Crystal Deformation

1. Slip Line Distribution

The visual result of translation gliding is the occurrence of a set (or sets) of parallel slip lines or bands on the surface of the crystal, visible under slight magnification. Schmid and Boas (8) were among the first to utilize this technique of slip system determination.

According to the orientation of the surface with respect to the glide direction, slip lines are long and straight* (surface is almost parallel to the slip direction) or branched and interconnected (surface makes an angle with the slip vector). No slip lines appear when the surface is exactly parallel to the glide planes, because no steps are formed on it.

Often one observed that superposed on the slip line pattern, kink bands which are zones approximately normal to the glide lines on which they show a slight curvature. In general, the slip line pattern of many materials depends strongly on the amount of strain, temperature

* This does not apply to the BCC class of metals.
2. Etch Pit and Decoloration Techniques

Promising methods to obtain direct optical evidence of the presence of dislocations in both metals and non-metals include thermal, chemical, or electrolytical etching of polished surfaces of deformed crystals. Depending on the nature of the etchant and the technique utilized, few or many etch pits, bounded by crystallographic planes, can often be observed on these faces. In deformed metals, these pits usually group near the zones which were indicated by glide lines before etching. Hence it was generally concluded that such etch pits indicate sites where dislocations meet the surface. However, it has not been possible up to now to prove that the correspondence between etch pits and dislocations is one to one, that is, that each pit corresponds to a dislocation and that each dislocation produces an etch pit. This difficulty has yet to be fully resolved but recent experimental work on mechanical twinning in calcite (23, 24, 25, 30, 31) suggests that such a correspondence does exist.

Keith and Gilman (23), using the etchant technique, succeeded in
observing the motion of individual dislocation lines in calcite. After a given deformation, etch pits were developed along the slip lines and the succeeding deformation, followed by renewed etching, revealed new, smaller pits, along the same slip band but were displaced from the old set of etch pits. The old etch pits had developed a flat bottom. Matching of etch pits on opposite sides of cleavage surfaces indicated that the defects were dislocations. Their study enabled the determination of the slip plane but not the slip direction. However, a knowledge of the direction of dislocation movement (as revealed by re etching) should permit a slip direction determination.

3. External and Internal Rotation Phenomena

a. External Rotation of the Crystal Lattice

During the process of slip in a constrained crystal, the lattice rotates relative to the axes of applied stress.

In an extension experiment of a single crystal oriented in the stress field such that only a single slip system will be activated, the lattice rotation consists in a movement of the longitudinal axis towards
the glide direction, during which the longitudinal axis always remains in
the plane determined by its original position and the direction of glide.

The magnitude of the external rotation can be obtained from the relationship,

\[ 1 + \varepsilon = \frac{L_f}{L_o} = \frac{\sin \chi_o}{\sin \chi_f} \]  

(1)

where: \( \varepsilon \) is the strain determined from measurements of the initial and
final lengths \( (L_o \text{ and } L_f \text{ respectively}) \) of the specimen, \( \chi_o \) and \( \chi_f \) are the
angles between the glide plane and directions of extension both before
and after the extension. (see fig. 1)

In the compression test, the lattice rotation consists of an approach
of the longitudinal direction to the pole of the glide plane. It follows
that the line of intersection of the glide plane with the compression
plates retains the same inclination to the crystal axes throughout the ex-
periment. Letting \( \chi_o \) and \( \chi_f \) again representing the angles between the glide
plane and the longitudinal direction before and after the compression, we
find

\[ 1 - \varepsilon = \frac{L_f}{L_o} = \frac{\cos \chi_f}{\cos \chi_o} \]  

(2)
with \((x_f - x_o) = \Delta\), the magnitude of the external rotation.

Finally, several geometrical relationships (8, 21) are observed during the formation of kink bands. We assume that slip is restricted to only one system and that the slip planes are nearly normal to the kink band boundary (Figure 4).

a. There is an external rotation of the lattice within the kink band with respect to that outside the band about an axis which is the intersection of the slip plane and the kink band boundary (KBB). The slip direction is normal to the external rotation axis (ERA).

b. The KBB must be normal to both the slip plane \((T)\) and the slip direction \((t)\) at the inception of kinking.

c. In the absence of elastic distortions, the KBB must rotate with respect to the crystal lattice on both sides of the band such that a symmetrical relationship (i.e., compatibility of deformation) will be maintained, otherwise there will be slip of the same amount and opposite sense on each side of the boundary.
b. Internal Rotation of Preexisting Lamellar Structures

This technique has been developed by Turner as a method to determine the glide system operative during the deformation. To make full use of this technique a preexisting lamella (P in fig. 1) must be in existence before the deformation. During the course of the deformation, P will be rotated to a new position by gliding upon a set of parallel planes T.

Bell (3) has shown that, if the magnitude of the shear strain and the gliding system are known, then the angle of internal rotation can be calculated for any lamella rotated during the deformation by means of the equation,

\[ \cot \alpha - \cot \beta = s \sin \gamma \]  

(3)

where \( \alpha \) and \( \beta \) are the angles between the lamella and the gliding plane before and after the rotation (\( \beta \) always is the larger angle), \( \gamma \) the angle between the gliding direction and the axis of internal rotation (the axis of internal rotation is the line of intersection between the glide plane \( s \) and the lamella), and \( s \) the shear strain. The shearing strain \( s \) can be
calculated as follows:

\[
\text{Twin Gliding:} \quad S = 2 \tan \frac{\psi}{2}
\]

where \(\psi\) is the angle of shear (fig. 2).

**Translation Gliding**

1) Extension 
\[
1 + \varepsilon = \sqrt{1 + 2S_o s^2 \sin^2 \chi_o}
\]

2) Compression 
\[
1 - \varepsilon = \sqrt{1 - 2S_o s^2 \sin^2 \chi_o}
\]

with \(S_o\) being the coefficient of resolved shear stress.

There are several geometrical distinctions between internal and external rotation. These include (18)

a) External rotation of a lamella is always towards parallelism with the least principal stress direction.

b) Internal rotations of lamellae are always opposite in direction sense to that of the external rotation.

c) The axis of internal rotation is the zone axis of the zone defined by the gliding plane and a rotated lamella in all positions.
of rotation. This is to say that the poles of the glide
plane and the rotated lamella in all positions of rotation
will fall on a great circle when plotted on either the
stereographic or equal-area net.
Part II. Deformation Models of Calcite

A. Turner Model

To explain phenomena observable in experimentally deformed calcite marble, Turner et al. (33) undertook a detailed study of calcite single crystals subject to varying conditions of confining pressure and temperature. A brief summary of their results is as follows:

1. Twin gliding on $e_i$ parallel to $\langle 100 \rangle = \langle e_i : r_j \rangle$ ($i \neq j$), sense positive.* This mechanism was effective over the complete range of investigated conditions of $20^\circ$ to $800^\circ$C, and under 5,000 to 10,000 bars confining pressure.

2. Translation gliding on $r_i$ parallel to $\langle 110 \rangle = \langle r_i : f_j \rangle$ ($i \neq j$), sense negative. Under 5,000 bars confining pressure, $r_i$ translation was the dominant mechanism at $20^\circ$C, the "sole" mechanism at $300^\circ$ to $400^\circ$C, and continued to function at higher temperatures (14,33).

3. Translation on $f_i$ parallel to $\langle 110 \rangle = \langle f_i : r_j \rangle$ ($i \neq j$), sense negative. This mechanism operated at $20^\circ$C and 5,000 bars confining pressure and at temperatures above $400^\circ$C (33,14).

* Postive sense implies that the twin/slip direction is such that the material above the twin/slip plane moves toward the optic axis $= c_v$. 
B. Theoretical Model

1. Introduction

Because slip is anisotropic, it occurs more readily along certain crystallographic planes and directions than along others. Many investigations (8, 25, 34), have established that the slip direction is invariably that along which atoms of the same spatial orientation are most closely packed,* and that the slip surface is often an important crystallographic plane of dense packing. Both observations are substantiated by the dislocation theory of plasticity in which a dislocation is characterized by two quantities, the Burgers vector and the width of the dislocation. The strain energy of a dislocation (Part III) being proportional to the square of its Burgers vector and the core energy proportional to its width, the dislocation (edge, screw or mixed) will choose those planes and directions so as to minimize both quantities. This implies that both the Burgers vector and the width of the dislocation will be a minimum. For example, in the NaCl-type structure the slip directions are given by $1/2 \langle 110 \rangle$ (closest packed directions) and

* Experimental evidence suggests that the slip direction is always that of the closest packed direction regardless of whether the crystal exhibits metallic, ionic or covalent bonding.
the slip planes at room temperature are (110) and (100), and at higher
temperatures (~400°C), (111) and (110). All three are planes of dense
packing within the structure.

2. Symmetry and Structural Relationships Between NaCl and CaCO₃

The structure of calcite (D₃d, \( \frac{2}{m} \)), CaCO₃, is common to a
number of carbonates and nitrates, and may readily be described in terms of
its relationship to the sodium chloride structure (Figures 5a, b; 6).

Figure 5a illustrates the symmetry relationships existing in the NaCl-
type structure (O_h, \( \frac{4}{m} \)). Here the \( e_{i} = \{110\} \) (i = 1,2,3) and \( a_{i} = \{110\} \) (i = 1,2,3) are characterized by two fold symmetry, the \( r_{i} = \{100\} \)
(i = 1,2,3) by four fold symmetry, and the \( f_{j} = \{111\} \) (j = 1,2,3,4)
by three fold rotoinversion axes. If now the sodium and chlorine ions are
replaced by calcium and carbonate ions respectively, and the cubic structure
elastically distorted by a compression along [111],* the calcite arrangement
results with only the \( a_{i} \) and \( f_{4} = [111] \) retaining their corresponding
structural symmetry (Figure 5b).*

* This hypothetical compression along [111] will not alter the spacial
position or symmetry of the \( a_{i} \) or \( f_{4} \) axes.
** In the NaCl structure, the \( a_{i} \) and \( e_{i} \) are structurally equivalent whereas
in the calcite arrangement, they are not.
Figure 5

Equal Area Projections (Upper Hemisphere) Illustrating the Symmetry Relationships in the NaCl-Type Lattice (a) and the Calcite Structure (b)
Figure 6

Three Dimensional Representation of the NaCl (a) and the CaCO₃ (b) Lattices
Because of this close structural similarity, an investigation was undertaken to correlate, if possible, their known deformation systems \((3,7,24,33)\). Theoretical predictions for flow systems in calcite were also made by the consideration of the above criteria for dislocation energies. These results are listed in Table 2 below.

3. **Translation Gliding Model**

The translation gliding elements predicted by the theoretical model include translation on \(r_i, f_j, e_i, m_i\) \((i = 1,2,3; j = 1,2,3,4)\) parallel to \(1/2\ <110>\). The Burgers vectors \(\text{i.e., the minimum distance for a shear to identity}\) for dislocations \(\text{(Part III)}\) in this model have a magnitude of \(4.99\)\(\text{A}\) as compared with \(8.03\)\(\text{A}\) required for dislocations in the Turner model.

In the translation gliding model of NaCl, each glide direction \(12\) in number \) is characterized by two fold symmetry axes. Similarly, those predicted for calcite in the theoretical model also possess this property whereas the Turner glide directions do not. This observation appears to have a significant effect upon the number of possible twinning systems in the calcite structure.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Glide Plane</th>
<th>Glide Direction</th>
<th>Glide Plane</th>
<th>Glide Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALITE</td>
<td>$r_1$ (100)</td>
<td>(011),(0\overline{1}1)</td>
<td>$e_1$ (011)</td>
<td>(0\overline{1}1),(0\overline{1}1)</td>
</tr>
<tr>
<td></td>
<td>$r_2$ (010)</td>
<td>(101),(\overline{1}01)</td>
<td>$e_2$ (101)</td>
<td>(\overline{1}01),(10\overline{1})</td>
</tr>
<tr>
<td></td>
<td>$r_3$ (001)</td>
<td>(1\overline{1}0),(\overline{1}10)</td>
<td>$e_3$ (1\overline{1}0)</td>
<td>(\overline{1}10),(\overline{1}10)</td>
</tr>
<tr>
<td></td>
<td>$e_1$ (011)</td>
<td>(0\overline{1}1),(0\overline{1}1)</td>
<td>$f_1$ (\overline{1}11)</td>
<td>(110),(0\overline{1}1),(101)</td>
</tr>
<tr>
<td></td>
<td>$e_2$ (101)</td>
<td>(\overline{1}01),(10\overline{1})</td>
<td>$f_2$ (\overline{1}11)</td>
<td>(110),(011),(101)</td>
</tr>
<tr>
<td></td>
<td>$e_3$ (1\overline{1}0)</td>
<td>(\overline{1}10),(\overline{1}10)</td>
<td>$f_3$ (\overline{1}11)</td>
<td>(110),(0\overline{1}1),(101)</td>
</tr>
<tr>
<td></td>
<td>$f_1$ (111)</td>
<td>(1\overline{1}0),(0\overline{1}1),(\overline{1}01)</td>
<td>$f_4$ (111)</td>
<td>(1\overline{1}0),(0\overline{1}1),(\overline{1}01)</td>
</tr>
<tr>
<td>CALCITE</td>
<td>$r_1$</td>
<td>(011)</td>
<td>$r_2$</td>
<td>(101)</td>
</tr>
<tr>
<td>(Turner)</td>
<td>$r_3$</td>
<td>(1\overline{1}0)</td>
<td>$f_1$</td>
<td>(110),(101)</td>
</tr>
<tr>
<td></td>
<td>$f_2$</td>
<td>(110),(011)</td>
<td>$f_3$</td>
<td>(110),(101)</td>
</tr>
<tr>
<td></td>
<td>$f_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CALCITE</td>
<td>$r_1$</td>
<td>(0\overline{1}1)</td>
<td>$r_2$</td>
<td>(1\overline{1}0),(10\overline{1})</td>
</tr>
<tr>
<td>(T.M.)</td>
<td>$r_3$</td>
<td>(1\overline{1}0),(1\overline{1}0)</td>
<td>Same as $r_1$</td>
<td>\n</td>
</tr>
</tbody>
</table>
4. Twin Gliding Model

Previous studies of single crystal deformation have shown that the higher the initial symmetry, the less likely are twins, and conversely, crystals of low symmetry tend to exhibit a large variety of twins. Experimental evidence suggests that mechanical twinning of only one type occurs in cubic crystals (7,24), whereas orthorhombic crystals, for example, show four systems of mechanical twins. In the NaCl structure, mechanical twinning on $f_1 = \{111\}$ parallel to $<112>$ is possible, but twin gliding on either the $a_1$, $e_1$ or $r_1$ planes is "impossible".

Because some symmetry elements are "lost" (i.e., 2 fold axes parallel to the $e_1$) during the "transition" from the NaCl to CaCO$_3$ lattice, it is of interest to consider the possibility of new twinning systems (other than the $f_j = \{111\} <112>$ which carry over during the transition) introduced in CaCO$_3$. However, before the model is discussed, a resume of the twinning elements and the geometrical laws of twin gliding will be necessary.

* For these planes, the twinning shear greatly exceeds the shear required for translation gliding.
a. Twinning Elements

The elements of twin gliding include (Figure 2): $K_1$, the twin plane; $K_2$, the second undistorted plane; $\eta_1$, the shear direction; and $\eta_2$, the trace of $K_2$ on the deformation plane $S$. Any detailed description of twinning requires not only a specification of these elements, but also, a specification of $S$ and the crystallographic shear $s$.

b. Twin Gliding Types

If $K_1$ and $\eta_2$ are rational, then the twin is called one of the first kind ($K_2$ and $\eta_1$ may be rational or irrational). Similarly, twins of the second kind have $K_2$ parallel to a rational plane and $\eta_1$ parallel to a rational direction ($K_1$ and $\eta_2$ may be rational or irrational). If $K_1$, $K_2$, $\eta_1$ and $\eta_2$ are all parallel to rational elements, the twins are of the first and second kinds. If $K_1$ and $\eta_1$ are rational and $K_2$ and $\eta_2$, then we shall denote this as twinning of the third kind.

c. Geometrical Requirements of Twinning

A crystal must retain its lattice symmetry and structure during twinning, however, the macrosymmetry of the twin may be higher because of an additional symmetry plane ($K_1$) or symmetry axis, or because one of the
previous axes has become of higher order. Clearly, plane \( K_1 \) cannot be a symmetry plane of the crystal in a reflection twin* and \( K_1 \) cannot be normal to an evenfold axis. Similarly, the \( \eta_1 \) direction in an axial twin** cannot coincide with a two fold axis (7,24).

Application of these rules to the calcite lattice structure reveals the possibility of twin gliding on the following systems (Table 3; Figures 7, 8).

a.) Twin gliding on \( e_1 = \{110\} \) parallel to \(<100>\), sense positive, \( s = 0.695 \) with twinning elements \( K_1 = \{110\}, K_2 = \{100\}, \eta_1 = <100> \), \( \eta_2 = <100> \), \( S = \{110\} \). Reflection and Axial twinning.

b.) Twin gliding on \( r_1 = \{100\} \), both positive and negative sense.

1.) Positive sense. Twin elements \( K_1 = \{100\}, K_2 = \{111\} \), \( \eta_1 = \{110\}, \eta_2 = <211>, S = \{110\}, s = 2.065. Reflection twin only.

2.) Negative sense. Twinning elements \( K_1 = \{100\}, K_2 = \{111\} \), \( \eta_1 = \{110\}, \eta_2 = <211>, S = \{110\}, s = 0.63. Reflection twin.

c.) Twin gliding on \( f_1 = \{111\} \), sense negative.

1.) Twin elements \( K_1 = \{111\}, K_2 = \{100\}, \eta_1 = <211> \),
Diagrammatic Representation of the Calcite Lattice Illustrating Twin Gliding on the e₁ and r₁ Planes in the Positive Sense. Sections are Normal to the a₁ Axis
Figure 8

Twin Gliding on the $r_i$ and $f_i$ Planes in the Negative Sense
Table 3

Prediction of Twinning Elements in Calcite

<table>
<thead>
<tr>
<th>Plane</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_1^{(+)}$</td>
<td>(011)</td>
<td>(100)</td>
<td>[100]</td>
<td>[011]</td>
<td>0.695</td>
</tr>
<tr>
<td>$r_1^{(+)}$</td>
<td>(100)</td>
<td>(111)</td>
<td>[011]</td>
<td>[211]</td>
<td>2.065</td>
</tr>
<tr>
<td>$r_1^{(-)}$</td>
<td>(100)</td>
<td>(111)</td>
<td>[011]</td>
<td>[112]</td>
<td>0.630</td>
</tr>
<tr>
<td>$f_1^{(-)}$</td>
<td>(111)</td>
<td>(100)</td>
<td>[112]</td>
<td>[011]</td>
<td>0.630</td>
</tr>
<tr>
<td>$f_1^{(-)}$</td>
<td>(111)</td>
<td>irrational</td>
<td>[011]</td>
<td>irrational</td>
<td>2.564</td>
</tr>
</tbody>
</table>
2.) \( k_1 = \{111\} \), \( \eta_1 = \langle 011 \rangle \), \( k_2 \) and \( \eta_2 \) both irrational, \( s > 2.0 \). **Reflection twin only.**

Although mechanical twinning involving shears greater than one have never been experimentally produced, petrographic analysis (33) of previously deformed calcite single crystals confirms positive \( r_1 \) twinning with a crystallographic shear of 2.065 occurring at stress differences on the order of 150 to 250 bars, although the crystallographic elements of \( r_1^{(+)} \) twinning were not determined (33).

5. **Summary and Discussion**

From an examination of the flow mechanisms in calcite suggested by the Turner and theoretical models, the following generalizations may be made.

a.) There is no correspondence between the predicted glide directions with those given by Turner. Rather, the slip directions in the Turner model become the twinning directions in the theoretical model.

* A reflection twin is a twin system in which the operation required to bring the lattices back into coincidence is one of reflection at the twin plane.
** An axial twin has the property that the lattices can be brought back into coincidence by a rotation through an angle which is characteristic of the particular crystal structure.
b.) The predicted glide directions correspond to those observed in the NaCl structure (i.e., they lie parallel to 2 fold axes) with the exception that half the slip directions existing in NaCl are "lost" in the "transition" to the calcite structure. The "lost" glide directions (those which have lost their 2 fold symmetry) become twinning directions in the calcite lattice.

c.) In the theoretical model, each glide plane possesses a dual character, namely that each plane possesses both slip and twinning directions normal to each other.

d.) The predicted twin systems can easily be shown to be derivable from the theory for mechanical twinning as developed by Jaswon and Dove (24).

e.) The theoretical flow mechanisms adhere to the space group requirements of the calcite lattice, whereas the Turner elements do not.

Because the predicted twinning directions are identical with the slip directions postulated by Turner, the question arises (assuming for time being that the Turner model adequately describes the deformation) as to the possibility of slip and twinning occurring in the same direction.
within the same crystallographic plane. Review of the literature (3, 7, 8, 24, 34) reveals that monoclinic KClO$_3$ (C$_{2h}$, $\frac{2}{m}$) can undergo slip and twinning in the same crystallographic plane and direction, the gliding elements being {001} and {100}. Experimental deformation of this material shows that translation gliding occurs far more extensively than twin gliding**, the reason being that the shear for twinning (i.e., the Burgers vector for a twinning dislocation) is larger than the shear required for a lattice repair distance. In calcite, translation on $r_1$ and $f_1$ parallel to $\{110\}$ requires a lattice shear of 8.08Å whereas the shear required for twin gliding is only 1.95Å and 4.20Å respectively. This suggests that twinning should occur with greater ease than translation.

In conclusion, the success of either model rests upon its ability to predict the mechanisms involved during the process of twinning on the known twin systems (e.g., $r_1$, $r_1$, $f_1$). In the following section, it will be shown that twinning on these planes can be adequately explained only by the mechanisms predicted by the theoretical model.

* The reason for the polarity in slip is due to an asymmetry of the ClO$_3$ group which results in a displacement on the center of symmetry of the $\delta_3$ group.

**Twinning in this crystal results primarily from strain hardening due to slip.
Part III. Dislocation Study of Calcite Deformation

A. Theoretical Studies of the Two Models

1. Structural Properties of Total Dislocations in Ionic Crystals

a. Introduction

In ionic crystals, the condition of electrical neutrality effects not only the dislocation geometry, but also its physical properties. In this case, the structure of an edge dislocation (or a dislocation with some edge character) is no longer determined by the criterion of least elastic energy, but also by the stringent condition that the "additional half-plane" does not disturb the charge neutrality in the crystal. For example, in ionic crystals having the NaCl structure, slip occurs in the 110 directions. Slip in these directions allows the minimum translation across a slip plane which restores the structure to its original order and does not bring like-charged ions closer together. As a result, the translations do not result in any long ranged electrostatic forces.

b. Comparison of Edge Dislocation Structures in the Two Models

It is well-known that when a single dislocation is symmetrically placed in an otherwise unstrained lattice, it will be subjected to no force.
However, if the dislocation is slightly displaced from such a position, the displacement will be opposed by forces set up on the glide plane because the atoms (on opposite sides of the glide plane) are no longer lying in equilibrium positions in the periodic force field of the plane. Near the dislocation core, the atoms are sheared out of their equilibrium positions since they have either started or nearly finished the slip process which takes them from one equilibrium position to the next. Those atoms ahead of the dislocation repel it backwards since they can return to the original lattice positions if it moves away from them and the atoms just behind the dislocation push it forward in order to reach the next set of lattice positions.

Figures 9a,b indicate the slip processes associated with pure edge dislocations in calcite (slip plane = r_1) for both the Turner and the theoretical model. In the Turner model, two additional half planes are necessary to ensure charge neutrality, whereas only one extra half-plane is required in the theoretical model. In both models, the extra half planes end at equal heights above the glide plane and the dislocation lines are characterized by charge neutrality.
Figure 9

Schematic Construction of Pure Edge Dislocations in the Turner Model (a) and the Theoretical Model (b)
As an example of the mechanisms involved for the movement of a dislocation, consider the three atoms nearest the center of the edge dislocation depicted in Figure 9b. Letting $A_1$ denote the atom (CO$_3$ group) forming the edge of the incomplete atomic plane, $A_2$ the atom below and to the right of $A_1$, and $A_3$ the atom below and to the left, it is clear that $A_1$ is not in a stable position for both $A_2$ and $A_3$ desire $A_1$ as a normal nearest neighbor. If now a shear stress is applied in the sense indicated, $A_1$ will be pushed to the left (similarly $A_3$ to the right) such that $A_3$'s claim on $A_1$ is favored whereas that of $A_2$'s lessened. Eventually (assuming the shear stress is of an adequate magnitude), $A_1$ and $A_3$ will join as indicated.

For dislocations in the Turner model (Figure 9a), it is apparent that dislocation movement should be considerably more difficult owing to the fact that for "equilibrium" (under the shear stress indicated), $A_1$ and $A_2$ must be joined to $A_6$ and $A_5$ rather than to $A_3$ and $A_4$, respectively. In this model, the equilibrium form of the dislocation suggests that not only will there be considerable distortion of the lattice in the vicinity of the dislocation, but also, an unsymmetrical rotation of the CO$_3$ groups.
will be necessary (i.e., the magnitude of the rotation will vary along the dislocation half-plane). These difficulties do not arise for dislocations in the theoretical model.

c. Critical Shear Stress to Move Dislocations in the Two Models

There have been many theoretical attempts to determine the magnitude of the CRSS required to initiate plastic deformation in crystalline materials. The chief difficulty arises from the fact that to calculate the force required, we need to determine the energy of misfit between the faces of the slip plane and then examine as to how this energy varies as the dislocation moves from one position of symmetry to the next. This energy of misfit is given by the summation of all the energies of interaction between the atoms facing one another across the slip plane.

It is well established that if the displacement field due to the dislocation at any arbitrary site is known, then the complete "stress" field as a result of the crystal dislocation can be calculated. Nabarro (8, 34), extending the theory developed by Peierls, and taking into account the discrete atomic structure, has shown that the strain energy of a dislocation depends on its position relative to the surrounding lattice planes.
By letting $\mathbf{a}$ represent the positions of the dislocation axis from the nearest position of symmetry, Nabarro showed that the displacement of the various atom rows (labelled by the index $n$, where $n$ increases away from the dislocation axis) is given by

$$ U_n = -\frac{b}{a\pi} a\tan \frac{2(n+\frac{1}{2}+\eta)}{a} b(1-r) $$

(7)

where $a$ is the lattice spacing along the dislocation. Carrying out the summation, it can be shown (8) that the strain energy per unit length of the dislocation is approximately,

$$ \psi = \frac{Gb^3}{2\pi(1-r)a} e^{-\frac{3\pi}{1-r} \left( \frac{a}{b} \right) \cos \frac{4\pi n}{3} \alpha } $$

(8)

which is a periodic function of the dislocation position. Taking $-(\ )$ we can determine the "Pierels force" (per unit length of dislocation line) opposing the glide motion of the dislocation in the crystal lattice:

$$ U_P = \frac{Gb^2}{(1-r)a} e^{-\frac{3\pi}{1-r} \left( \frac{a}{b} \right) \sin \frac{4\pi n}{3} \alpha } $$

(9)

This is a maximum when $\alpha = \frac{1}{4} \sin^{-1} \left( \frac{1}{2} \right)$ or

$$ F = U_P \max = \frac{Gb^2}{(1-r)a} e^{-\frac{3\pi}{1-r} \left( \frac{a}{b} \right) } $$

(10)

The chief advantage of the above theory is that it takes into account the periodic nature of the crystal and yet it is simple enough
to apply to imperfect crystals. Similarly, this theory collaborates with the experimental evidence that slip occurs on close packed planes in the closest packed directions. The chief criticisms of the theory concern the periodic shear stress law which appears to be a poor approximation for real crystals. This approximation causes the width of the dislocation to be underestimated. Also the theory does not take into account the anisotropy of the medium nor the temperature effects on the slip systems. Therefore, at best, the theory serves as a rough approximation only.

Aside from the criticisms of this theory, it will be of interest to calculate the RATIOS of $\frac{F^{(T)}}{F^{(B)}}$ for both the Turner and the theoretical model. Neglecting the severe lattice distortion and the $CO_3$ rotations in the neighborhood of the dislocation core in the Turner model, we find

$$\frac{F^{(T)}}{F^{(B)}} = \left( \frac{b_T}{a_T} \right)^2 \left( \frac{Q_T}{G_T} \right) \left[ \frac{Q_T}{b_T} - \frac{G_T}{b_T} \right] \ldots \text{ (11)}$$

For glide on the $r_1$ plane, $a_B = a_T = 3.21\text{A}; b_T = 8.08\text{A}, b_B = 4.99\text{A}$, and letting $\nu = 0.3$ gives

$$\frac{F^{(T)}}{F^{(B)}} \approx C \left( \frac{2a}{2b} \right)^2 \ldots \text{ (12)}$$

or $F^{(T)} = 24.1 F^{(B)}$ implying that the "stress" required to move a dislocation in the Turner model will be 24 times that required for a dislocation
in the theoretical model.

2. Elastic Energies of Total Dislocations in the Models

a. Introduction

Dislocations are not thermodynamically stable; that is, their presence increases the free energy of the crystal. It is usually impossible to eliminate them from the crystal lattice completely, and those which remain tend to assume configurations such that their total energy is minimized. Considerations of dislocation energies, for example, can explain not only why low stress levels are required to initiate plastic deformation and why crystalline materials strain harden with increasing strain, but also why dislocations in particular crystal structures find it energetically favorable to dissociate into extended dislocations.

Models for the creation and movement of dislocations can often be rationalized by considerations of the energies involved. In this section, we shall compare RATIOS of dislocation energies, both strain and core energies, both for the Turner and theoretical model.

b. Elastic Energies of Edge and Screw Dislocations

As has been previously indicated, there is a field of distortion
around each dislocation which can be subdivided into two zones: 1) the nucleus (core), or the distorted material; 2) the zone of stressed undistorted material. The dislocation core consists of material with large distortions of the lattice in which the atoms are considerably displaced from their normal positions. The distortions in the zone 2 satisfy Hooke’s law and therefore, on the basis of elasticity theory, a calculation of the stresses and energy due to the dislocation is possible.

The value of the tangential stress around dislocations is given by an infinite series of the form (34),

\[ \sigma = \sum_{n=0}^{\infty} \frac{b_{n+1}}{R^{n+1}} \]

where \( R \) is the distance from the center of the dislocation. For reasonably large distances from the core, where \( (R/b) \) is large, the approximation,

\[ \sigma \approx \frac{b_0}{R} \]

is valid.

From the stress field of the dislocation, we can calculate the elastic energy in the crystal, by constructing the elastic energy density as a function of the space coordinates and then integrating over the volume from \( r_0 \), the core
radius of the dislocation, to \( R \), the effective radius where the stress field of the dislocation can be considered to be negligible.

The results for the edge and screw dislocation are:

\[
\text{Edge Dislocation} \quad E_e = \frac{GB_l^3}{4\pi(1-\nu)} \log \frac{R}{r_0} \quad \ldots \quad (15)
\]

\[
\text{Screw Dislocation} \quad E_s = \frac{GB_l^3}{4\pi} \log \frac{R}{r_0} \quad \ldots \quad (16)
\]

Assuming these equations give a fair approximation when applied to the calcite lattice, we find for the two models (superscripts \( T \) and \( B \) referring to the Turner and theoretical model respectively)

\[
\text{Turner Model} \quad \frac{E_e^{(T)}}{b_B} = \frac{GB_l^2}{4\pi(1-\nu)} \log \frac{R_T}{r_0} \quad \ldots \quad (17)
\]

\[
\text{Theoretical Model} \quad \frac{E_e^{(\omega)}}{\frac{1}{2}b_T} = \frac{GB_l^2}{4\pi(1-\nu)} \log \frac{R_B}{b_B} \quad \ldots \quad (18)
\]

where the lattice spacing along the dislocation lines are \( b_B \) and \( 1/2b_T \) in the Turner and theoretical model respectively.

For \( r_1 \) glide, we have that \( R_B \equiv 1/2 \, R_T \), \( R_B \equiv 1/2 \, R_T \), \( b_T = 8.08 \AA \), and \( b_B = 4.99 \AA \). Using these values and taking ratios of the above equations yields,

\[
\frac{E_e^{(\omega)}}{E_e^{(T)}} = 2 \left( \frac{b_T}{b_B} \right) \frac{\log \frac{R_B}{r_0}}{\log \frac{R_B}{r_0}} \quad \ldots \quad (19)
\]

or

\[
\frac{E_e^{(\omega)}}{E_e^{(T)}} \approx 3.58 \quad \ldots \quad (20)
\]
A similar result holds for the screw dislocation.

c. Core Energy

In comparison to the strain energy outside \( r \), the core energy forms but a small part of the total energy of the dislocation. It will suffice for the time being to make a rough estimation of this quantity.

The strain at a distance \( r \) from the dislocation being approximately \( \Sigma = \frac{b}{2\pi(1-\nu)\rho_0} \), we assume that the average strain inside \( \rho \) is \( \frac{2b}{2\pi(1-\nu)\rho_0} \).

If Hooke's law holds well enough for a rough estimate, then the energy of the center is approximately \( \frac{1}{3} G s b^2 \) per atomic plane, where \( s \) is the atomic spacing along the dislocation. Considering the two models, and taking ratios of the two energies, we find,

\[
\frac{E_c^{(1)}}{E_c^{(2)}} \approx 3.60 
\]

Estimates of the core energy in metals have been made by Bragg (8) who makes use of the criterion that the energy density in the core cannot exceed the latent heat of melting. Huntington (8) makes his calculation in NaCl by computing the electrostatic energy between atoms in a dislocation. All three of the above techniques arrive at the conclusion that the core energy is about one-tenth that of the strain.
energy field outside r.

d. Discussion

The preceding calculations constitute a strong argument in favor of the flow systems in the theoretical model. These equations fail, of course, to take into account the anisotropy of calcite and can, therefore, form only a rough approximation of the strain energy. However, these relations can afford a reasonable estimate if we consider ratios rather than their absolute magnitude.

For a dislocation in an anisotropic media, the general form of the strain energy function can be shown to be:

\[ \psi = \frac{1}{4\pi} B_{ij} b_i b_j \log \frac{R}{r} \quad \ldots \quad (22) \]

where \( B_{ij} \) is a function of the orientation of the dislocation with respect to the principal axes and the elastic constants of the material. Preliminary theoretical work shows that if we consider ratios for the two models that:

\[ \frac{\psi^{(T)}}{\psi^{(B)}} = \frac{B_{ij}^{(T)} + B_{33}^{(T)}}{B_{ij}^{(B)}} \left( \frac{b_i}{b_j} \right)^2 \quad \ldots \quad (23) \]

with the restraint that \( B_{11}^{(T)} + B_{33}^{(T)} \geq 2 B_{22}^{(B)} \) with equality in the isotropic case only. Thus the strain energy due to dislocations in the theoretical model is less than that in the Turner model.
B. Extended Dislocations in the Calcite Lattice

1. Structural Background

In calcite, the planes of all the $\text{CO}_3^2-$ groups are parallel and normal to the triad axis of the rhombohedral cell. This group consists of a central carbon atom with the three $\text{O}^2-$ atoms at the corners of an equilateral triangle with a C-O distance of about 1.24Å and the three oxygen atoms about 2.3Å apart. The coordination of the structure is such that each $\text{Ca}^{+2}$ ion is surrounded by a somewhat irregular octahedron of six $\text{O}^2-$ neighbors, while each $\text{O}^2-$ ion is bound to two $\text{Ca}^{+2}$ ions as well as to the $\text{C}^{+4}$ ion of the carbonate group.

It is well-known that the number of octahedral interstices in a hexagonal closest packed structure or framework is equal to the number of spheres which define the framework. Figure 10(a,b) shows that the interstices of the calcite structure lie on planes midway between contiguous closest packed planes of the framework, and that the positions within such a plane define a simple hexagonal mesh. Figure 10b illustrates the normal distribution of $\text{CO}_3^2-$ ions on the mesh, implying that the arrangement of filled and empty interstices is an ordered one. It is clear that the
Figure 10

Basal Plane of Calcite Illustrating the Hexagonal Close Packing of the O₃ Groups with the C and Ca Ions Filling the Interstices
hexagonal meshes of interstices must be directly above or below one another, i.e., the interstices must lie on the points of a simple hexagonal lattice.

It is necessary to note that the ordered positions of the holes define a hexagonal mesh which is a multiple of the corresponding one determined by the CO$_3$ groups. In addition, the two meshes (i.e., the CO$_3$ mesh and the Ca mesh directly above it) differ in orientation by a rotation of $30^\circ$ about the mesh normals, implying that the directions of closest packing of each ionic group (of the SAME SPATIAL ORIENTATION) have the indices $\langle11\bar{2}0\rangle = \langle1\bar{1}0\rangle$.

2. Extended Dislocations in the Calcite Structure

a. Introduction

According to dislocation theory, the self-energy of a dislocation is proportional to the square of its Burgers vector, $b$. Thus for any given plane, slip must be in the direction of the Burgers vector of that total dislocation which has the shortest possible Burgers vector and the Burgers vector of a total dislocation must correspond to a STRUCTURAL REPEAT TRANSLATION.
A total dislocation lying in a close-packed plane can lower its energy by dissociating into an extended dislocation composed of partials, with individual Burgers vectors shorter than that of the parent dislocation, separated by a region of faulted structure. Dissociation will occur only if the energy gained by going to the shorter Burgers vectors is not counterbalanced by an increase in the strain energies of the partial dislocations.

The question of whether a total dislocation in calcite can dissociate is a particularly important one. There are several reasons for asking the question. In the first place, the Burgers vector of the total dislocation is considerably greater than those of the several kinds of partials that are readily suggested by the nature of the structure. Secondly, we know that dissociation of total dislocations does occur in structurally related close-packed metals (Mg, Cd, Zn, etc.). Moreover, detailed examination of Figure 10 shows that the TOTAL DISLOCATION in motion must cause the moving CO$_3$ groups (and Ca ions) of any one layer to climb directly over those below and, as a result, disrupt the close-packed character of the structure. Obviously, such a climbing motion should be unfavorable because of the like charges coming into "contact".
A brief discussion of the properties of the stacking faults introduced by the dissociations appears to be warranted at this point. For purposes of illustration, the following shorthand notation will be used to describe the packing sequence in calcite.

If we let

\[ \begin{align*}
A &= \text{CO}_3 \\
B &= \text{Ca} \\
C &= \text{CO}_3 \\
D &= \text{Ca}
\end{align*} \]

the packing sequence parallel to \((0001) = (111)\) will be given by

\[ \text{ABCDABCDA...} \]

As many of the properties of partial dislocations follow from the properties of stacking faults, it must be noted that a stacking fault can lie only on one plane. This implies that the partial dislocations giving rise to the stacking fault must also lie in the plane. For example, consider a total dislocation with Burgers vector \(1/2 [\text{II}0]\) and slip plane \((111)\). This dislocation is equivalent to two superposed partials with
Burgers vectors $\frac{1}{6}[211]$ and $\frac{1}{6}[121]$ respectively. The two partials are connected by a strip of stacking fault on the (111) plane and together they form an extended dislocation.

In the calcite arrangement, the dissociation reaction *

$$\frac{1}{2}[110] = \frac{1}{6}[121] + \frac{1}{6}[211] \quad (T = (111))$$

is structurally favorable. As a result of dissociation, the change in the stacking sequence is given by

\[
\text{Unsheared Portion} \quad \text{Sheared Portion}
\]

Examination of the final lattice structure shows that the resulting stacking fault is unsymmetrical in that the partials result in a movement of Ca ions into the slots previously occupied by the CO$_3$ groups and visa-versa, resulting in an electrostatic repulsion normal to the slip plane. In the unsymmetrical structure so produced, there are no interfacial deviations in the charge and bond distributions across the interface, but rather, the abnormalities are confined to the next-nearest neighbors.

This suggests that the electrostatic repulsion so introduced should be of

* Rhombohedral indices are utilized so as to facilitate the correspondance between the calcite structure to the FCC arrangement.
b. Dissociation Scheme

Analysis of Figure 10 suggests two types of dissociations on the basal plane are possible with one more favorable than the other. First, a splitting can be accomplished formally by choosing pairs of half-partial with $b = 1/2 \ [10\bar{1}0] = [2\bar{2}I] = 0.583 b_B$, where $b_B = 1/2 \ [1\bar{1}0] = 4.99 \text{A}$. Since this vector corresponds to a single Ca-Ca distance in a close-packed direction, it is identical with the Burgers vector of a total dislocation in a close-packed HCP metal. The second kind of splitting that is suggested is simply an additional subdivision of each of these partials so as to give a resultant of four quarter partials with $b = 1/6 \ [2\bar{2}I0] = 0.25 b_B$. However, this scheme has the disadvantage that two stacking faults are introduced as compared with only one in the former scheme.

Based on an energy viewpoint, each half-partial would have one third the self-energy of the total dislocation and each quarter partial, on the other hand, possesses only one-sixteenth the self-energy based on the $b^2$ criterion (Frank's rule) alone. In addition, there is the additional decrease in both schemes of the strain energy associated with the elimination
of the climbing of \( CO_3 \) groups (and Ca) over one another.

A tabulation of the possible dislocation dissociations possible in the calcite structure based on the total dislocation directions predicted by the theoretical model is presented below. For purposes of illustration, both rhombohedral and hexagonal indices are shown.

1.) **BASAL DISLOCATION DISSOCIATIONS** (Figure 11)

<table>
<thead>
<tr>
<th>Rhombohedral (pqr)</th>
<th>Hexagonal (hkil)</th>
<th>Plane of Stacking Fault</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 [110] = 1/6 [121] + 1/6 [211]</td>
<td>1/2 [210] = 1/2 [100] + 1/2 [010]</td>
<td></td>
</tr>
<tr>
<td>1/2 [011] = 1/6 [121] + 1/6 [112]</td>
<td>1/2 [121] = 1/2 [100] + 1/2 [010]</td>
<td></td>
</tr>
</tbody>
</table>

2.) **NON-BASAL DISLOCATION DISSOCIATIONS** (Figures 11, 12)

<table>
<thead>
<tr>
<th>Slip Plane</th>
<th>Rhombohedral</th>
<th>Hexagonal</th>
<th>Stacking Fault Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>1/2 [011] = 1/6 [121] + 1/6 [112]</td>
<td>1/2 [210] = 1/2 [100] + 1/2 [010]</td>
<td></td>
</tr>
</tbody>
</table>

The following system of indexing has been used to facilitate the
reaction representation on the stereographic projection.

1.) $f_j$ ($i = 1,2,3,4$) Partials (Figures 11,13)

\[
\begin{align*}
A_1 & = 1/6[121] & A_6 & = 1/6[121] & A_{11} & = 1/6[211] \\
A_2 & = 1/6[112] & A_7 & = 1/6[121] & A_{12} & = 1/6[122] \\
A_3 & = 1/6[112] & A_8 & = 1/6[211] & A_{13} & = 1/6[211] \\
A_4 & = 1/6[211] & A_9 & = 1/6[112] & A_{14} & = 1/6[121] \\
A_5 & = 1/6[211] & A_{10} & = 1/6[121] & A_{15} & = 1/6[112] \\
\end{align*}
\]

2.) $r_i$ ($i = 1,2,3$) Partials (Figure 12a)

\[
\begin{align*}
B_1 & = 1/6[012] & B_3 & = 1/6[102] & B_5 & = 1/6[210] \\
B_2 & = 1/6[021] & B_4 & = 1/6[201] & B_6 & = 1/6[120] \\
\end{align*}
\]

3.) $e_i$ ($i = 1,2,3$) Partials (Figure 12b)

\[
\begin{align*}
\end{align*}
\]

c. Discussion

We have discussed dislocation dissociations based upon the theoretical model with no recourse as to the feasibility of dissociation based on the Turner model. Consideration of this possibility suggests that the dissociation of total dislocations with Burgers vectors $b_T = 8.08\AA$ are energetically unfavorable. For example, in the case of $r_i$ glide in the Turner model, the reaction

\[
b_T [110] = b [100] + b [010]
\]
Figure 11

Equal Area Projection of Dislocation Dissociations Reactions for Basal and \( f_1 \) Total Dislocations
Figure 12

Equal Area Projection for Dissociations for the \( r_i \) (a) and \( e_i \) (b)
Total Dislocations
Figure 13

$\{f_i\}$ Planes Illustrating the Angles Between Extended Dislocations
where $b = 6.41 \text{A}$, is structurally possible. However, application of Frank's $b^2$ criterion shows that $b_T^2 < 2b^2$ implying that dissociation will not occur.

C. Dislocation Theory of Mechanical Twinning in Calcite

1. Introduction

The arguments for a dislocation theory of mechanical twinning are the same as those for a dislocation theory of slip: namely that it is doubtful that all the atoms concerned should all move simultaneously, and that twinning occurs at stress levels far below the theoretical shear strength of a perfect lattice. It has been mentioned in Part I that a twinning dislocation must be a partial dislocation owing to the observation that the twinning translation is always smaller than the translation required for slip. This implies that the process of mechanical twinning must somehow involve the generation and movement of partial dislocations.

If Figure 3 is regarded as referring to an FCC lattice, the twinning dislocation depicted is in fact a Shockley half dislocation in that the twinning process replaces the cubic stacking by hexagonal packing over a width of two octahedral planes. To understand the process of twinning
in crystalline materials such as the above structure, it will be necessary to consider the mechanism of twinning from a dislocation viewpoint.

Figure 14a illustrates the process involved in mechanical twinning. Denoting the three straight dislocation lines meeting at a nodal point $0$ as $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$, it can easily be shown that the Burgers vectors $\vec{b}_1$, $\vec{b}_2$, $\vec{b}_3$ of the lines meeting at $0$ must satisfy the relation

$$\Sigma \vec{b}_n = \vec{0} \quad \ldots \quad (24)$$

As a simple example of the Frank Read mechanism of slip multiplication, if dislocation $\#3$ is a perfect dislocation, it can move in any plane $\hat{n}$ where $\vec{b}_3 \cdot \hat{n} = 0$, and if neither $\vec{a}_1$ or $\vec{a}_2$ lie in $\hat{n}$, then $\vec{a}_3$ can spiral in this plane producing increments of slip. If this process is to generate a multiplication of slip on this plane, then the vectors $\vec{b}_1$ and $\vec{b}_2$ must lie on this plane. However, if $\vec{b}_1$ and $\vec{b}_2$ do not lie on $\hat{n}$, then a component

$$\vec{r} = (\vec{b}_1 \cdot \hat{n})\hat{n} = (-\vec{b}_2 \cdot \hat{n})\hat{n} \quad \ldots \quad (25)$$

exists normal to $\hat{n}$ and the dislocation $\vec{a}_3$ will be displaced by $\vec{r}$ for each revolution it makes about $\vec{a}_1$ (or $\vec{a}_2$). Hence the sweeping dislocation generates a helical surface of slip if $\vec{r}$ is identical to a lattice spacing.
Figure 14

Illustration of Twinning Dislocation Mechanism
normal to the slip plane \( \mathbf{n} \).

In the case where the sweeping dislocation \( \mathbf{a}_j \) has a Burgers vector of magnitude sufficient to produce the correct shear displacement to generate a twinned structure, the following conditions are necessary to create a homogeneously twinned crystal: (7,8)

a.) The Burgers vectors of the pole dislocations must possess components normal to the twin plane \( K_1 \) which is **equal** to the lattice spacing of these planes.

b.) The pole dislocation should be of the sessile type.

c.) The twinning dislocation and pole dislocations must form a node and the twinning dislocation must be glissile in the \( \mathbf{n} \) plane which is intersected by the poles.

As an example of the above twinning scheme, consider the process of mechanical twinning in the BCC lattice (8). It has previously been shown that twins can be formed in this structure by a shear of magnitude \( 1/\{2 \} \) in the \( \langle 111 \rangle \) direction on the \{112\} planes. If the line AOB (Figure 14b) in this crystal represents a unit dislocation with Burgers vector \( 1/2 \ [111] \),
then, supposing sufficient energy is available from external sources, a
dissociation

\[ \frac{1}{2} \langle 111 \rangle = \frac{1}{3} \langle 112 \rangle + \frac{1}{6} \langle 11\bar{1} \rangle \]

may occur along part of the dislocation line. As \( \frac{1}{6} \langle 111 \rangle \) is glissile
within the potential twin planes \((112),(121),(211)\), this
dislocation can branch away from AOB and form OC where it can rotate
about the nodal point 0. Dislocation OB is then left with a Burgers Vector
\( \frac{1}{3} \langle 112 \rangle \) which is sessile in the \((112)\) plane. The Burgers vectors of
the dislocations along AOB have a component \( \frac{1}{6} \langle I21 \rangle \) normal to the twin-
ning plane \((I21)\) equal to the lattice spacing of these planes. Thus, the
node at 0 can produce twinning on \((I21)\) if, under a suitable stress, OC
rotates about AOB.

2. Development of the Calcite Twinning Model

a. \( a_1 \) Twinning

It is well-known that a twinned structure can be formed in calcite
by a shear of 0.695 in a \(<100>\) direction (+ sense) on a \( \{11\bar{1} \}\) plane.

Consider a portion of a line of perfect dislocation of \( \frac{1}{2} \langle 01\bar{1} \rangle \) type
which lies on the (111) plane. Then, as discussed above, a dissociation of the type

$$\frac{1}{2} [011] = \frac{1}{6} [112] + \frac{1}{6} [121] \quad \cdots \ (R1)$$

can occur along a part of this line. Similarly, a dissociation

$$\frac{1}{2} [011] = \frac{1}{6} [112] + \frac{1}{6} [121] \quad \cdots \ (R2)$$

may take place for a dislocation line on a \( f = (111) \) plane. Such disociations may either be initially in the crystal as a result of growth or they may, perhaps, be due to an applied stress. The interactions of dislocations may result in the formation of fresh defects in the crystal lattice. If the dislocation interaction is determined only by forces of long range order, then, as a first approximation, it is sufficient to make use the Frank criterion (i.e., two dislocations repel each other if their Burgers vectors make an acute angle and attract each other forming another dislocation if the angle is obtuse). Use of Frank's rule shows that the combination

$$\frac{1}{6} [112] + \frac{1}{6} [112] = \frac{1}{3} [100] \quad \cdots \ (R3)$$

is energetically feasible. The resultant dislocation, \( \frac{1}{3} [100] \), by def-
inition, is a pure screw dislocation in that the dislocation line is normal
to the slip direction 1/2 [011].

The Burgers vector of the twinning dislocation 1/3 [100] is given by

\[ b_e = (\frac{2.5}{\cos 30^\circ} \cos 63^0) + (\frac{2.5}{\cos 35^\circ} \cos 62^0) \]
\[ = 2.655 \, \text{Å} \]

as compared with the geometrically determined value of \( b_e = s_e d_e = 2.65 \, \text{Å} \).

The strength of the components of the Burgers vectors normal to (011) is, for both the 1/6 [112] and 1/6 [112] dislocation,

\[ \frac{1}{2} d_e = 2.87 \cos 77^\circ + 3.05 \cos 67^\circ = 1.87 \, \text{Å} \]
\[ d_e = 3.74 \, \text{Å} \]

This compares with the value \( d_e = 3.814 \, \text{Å} \) as determined from the crystal structure. As the angles above were calculated with the equal-area projection, the correspondence between these values is remarkable.

The dislocation 1/3 [100] can glide in the (011) plane and in so doing, it can easily be shown that this dislocation produces a twinning shear of the layers between which it passes. Similarly, the dislocations 1/6 [112] and 1/6 [112] form a suitable pole for twinning on (011) if, under the action of a suitable stress, it rotates about the nodal point defined by the intersection of the three dislocations.
b. $r_1^{(+)}$ Twinning

As discussed in Part II-B, twin gliding on $r_1$ in the 110 directions ( (+) sense ) requires a crystallographic shear of 2.034. As the spacing of the $r_1$ planes is 3.026Å, the Burgers vector of a twinning dislocation must have a magnitude of 6.155Å.

Experimental evidence (33) shows that the frequency of $r_1^{(+)}$ twinning, although occurring under low stresses ( about 250 bars ), is far less in comparison to twin gliding on $e_1^{(+)}$. Petrographic analysis of deformed calcite crystals suggests that $r_1^{(+)}$ twins are connected with the development of the $e_1^{(+)}$ twins. This implies that perhaps the interaction of $e_1^{(+)}$ twinning dislocations and other dislocations within the lattice may be responsible for the generation of $r_1^{(+)}$ twinning.

If we consider the reactions,

$$
\frac{1}{3} [010] + \frac{1}{6} [121] = \frac{1}{6} [101] \quad \cdots \quad (R4)
$$

$$
\frac{1}{6} [211] + \frac{1}{6} [101] = \frac{1}{6} [110] \quad \cdots \quad (R5)
$$

Frank's rule of dislocation interactions shows that reaction R5 is energetically favorable in that both terms on the left-hand side of the equation form an acute angle with each other.

The Burgers vector of the dislocation $1/6[101]$ is then
\[ b_{1/6[101]} = 2.88 \cos 45^\circ + 2.65 \cos 71^\circ = 2.902 \text{Å} \]

and that for \(1/6[211]\),

\[ b_{1/6[211]} = 2(2(2.65 \cos 52^\circ) \cos 38^\circ) = 5.166 \text{Å} \]

The Burgers vector of the twinning dislocation \(1/6 \{110\}\) is then

\[ b_{1/3}(+) = 2.902 \cos 42^\circ + 5.166 \cos 39^\circ = 6.17 \text{Å} \quad \ldots \quad (29) \]

while the strength of the Burgers vectors normal to \((001)\) being

\[ d_{1/3}(+) = 2.902 \cos 75^\circ + 5.166 \cos 61^\circ = 3.24 \text{Å} \quad \ldots \quad (30) \]

These results agree reasonably well with the calculated values above.
3. Energies of Coherent Twin Boundaries in Calcite

It is well-established that the formation of twin layer nuclei in monocrystals depends on the surface energy, $\Sigma_0$, of the coherent twin boundary. During the formation of a twin layer, the sweeping twinning dislocation moves away from the other dislocations and leaves in its path a layer of stacking fault. Clearly, the extra energy of this fault causes a force (i.e., a back stress opposing the applied stress) on the sweeping dislocation. When the distance between the dislocations exceeds a few atomic spacings, the energy of the stacking fault is proportional to its area and if the energy per unit area of the fault is $\Sigma$, then the forces per unit length on the dislocations are also $\Sigma$. This force is equivalent to a shear stress,

$$\tau = \frac{\Sigma}{b} \quad \text{... (31)}$$

where b is the strength of the twinning dislocation acting on the sweeping plane against the direction of the shear displacement caused by the dislocations.

Unfortunately, little is known of the absolute magnitude of $\Sigma$, except that it is much smaller than typical grain boundary energies (8).
Fullman (8) obtains for the energy of a coherent twin boundary in Cu the
value $\Sigma = 20\text{ergs/cm}^2$. This is compared to $\gamma = 400\text{ergs/cm}^2$ for a typical
grain boundary energy of Cu.

As a first approximation, it will be of interest to use equation
31 to calculate the surface energies of coherent twin boundaries in calcite
for both $e_1^{(+)}$ and $r_1^{(+)}$ twinning. Experimental work by Turner et al. (33)
has shown that the shear stresses required to initiate $e_1^{(+)}$ twinning is
approximately 100 bars and that for $r_1^{(+)}$ twinning about 250 bars. Thus
the stacking fault energies of the $e_1^{(+)}$ and $r_1^{(+)}$ twins are roughly
2.65 and 15.37 ergs/cm² respectively.

A rough estimate of the time to form a twin layer is warranted.

By analogy with the F-R mechanism of dislocation multiplication, it is known
that as the sweeping twinning dislocation spiral builds up, the spiral
makes $v/2\pi l$ turns per second where $v$ refers to the velocity of the dislocation
normal to itself and $l$ refers to twice the limiting radius of curvature
about which a section of the dislocation line can be "bent" by an appro-
priate stress. For each revolution of the twinning dislocation, one layer
of twin is added to the crystal. Taking $l = 2(G/\tau)b$ as a first approximation, we find for $e_{1}^{(+)}$ twinning that $l = 2.6 \times 10^{-4}$ cm. Therefore, the time necessary for the twin to grow by one atom layer is approximately $8 \times 10^{-2}$ microseconds for a limiting velocity of $v = 10^4$ cm/sec. A similar result holds for $r_{1}^{(+)}$ twinning.

4. Discussion

The development of a relatively simple dislocation model of mechanical twinning on $e_{1}^{(+)}$ and $r_{1}^{(+)}$ has been accomplished which satisfies the stringent geometrical requirements for mechanical twinning. The values of the stacking fault energies are reasonable and are of the same order of magnitude with those previously determined in the metallic crystals.
D. Etch Pit Studies of Deformed Calcite

1. Introduction

As the geometry and external symmetry are an indication of the mechanisms involved during the growth of the crystal, so also when a crystal is attacked by suitable solvents, the initial dissolution phase often takes place in a manner related to the point group symmetry of the underlying structure. Invariably, the etching action starts sporadically at various points on the crystal faces and is initiated along dislocation lines in the structure, although most etching solutions are sensitive to defects in the crystal other than dislocations. However, at these defects, the etch pits produced are flat-bottomed and can easily be distinguished from the pointed pits which appear at dislocations.

The symmetry of each etch figure appearing on a crystal face should conform to the symmetry elements of the point group normal to that crystal face. Therefore, the etch pit symmetry should be one of the ten plane point groups illustrated in Figure 15. Furthermore, the relationships between the shapes and placement of the pits on the various crystal faces should conform to the symmetry relations of these faces. The general shapes of etch figures
Figure 15

The Ten Crystallographic Point Groups
Figure 16

Typical Etch-Pit Figures Appearances on Hexagonal Crystals with $\overline{3}$ (a) and $6\overline{2}2$ (b) Axes
for various symmetries and their relationship to each other are shown in Figure 16.

2. Development of Dislocations in Calcite

Keith and Gilman (21), etching calcite cleavage flakes with various concentrations of formic and acidic acid, have observed that the orientations of the etch figures differ for the two acids: the pits formed by formic acid (rectangular in outline) having edges approximately parallel and normal to [101] (observation plane (010)) whereas those produced by acidic acid are parallel and normal to [100]. After verifying that the etch figures result from dislocations (i.e., a one-to-one correspondence between the pits on both sides of the cleavage plate), they subjected the cleavage flakes to a three point loading at varying temperatures (20° to 600°C) and found evidence of translation gliding on both (100) and (111) with inconclusive evidence of gliding on (110). However, their technique said nothing about the glide directions.

Bengus et al. (24), using a 10% aqueous solution of tartaric acid with an optimum ratio of $v_n/v_s = 0.14$, where $v_n$ and $v_s$ are the speeds of
etching normal and parallel to the cleavage plate, have carried the etching study a step further by using interference patterns of individual etch pits to determine the directions of the dislocation lines. After comparing the patterns for a few etch pits, they established that the dislocation lines lie in the crystallographic direction $[11ar{2}]$. If this is true, then these pits must represent the emergence of edge dislocations lines with Burgers vectors $4.99\text{Å}$ lying in the basal plane.

3. Dislocation Interaction in Calcite Twinning

Recently a number of papers have been published (25,30,31), in which etch figures in mechanically twinned calcite were studied. As a rule, these authors have concluded that distortions are present not only in the parent and twinned regions, but also, on the boundary between the two zones in the crystal. It follows as a necessary consequence that the existence of a boundary between a twin lamella and the parent crystal results in an increase in the free energy of the crystal. Macroscopically, this increase is due to the increase in chemical potential of the particles situated on the boundary and on the microscopic viewpoint, such an increase is explained by a variation in the bond forces of particles situated in the boundary zone.
An interesting observation by Startsev et al. (24) is that twin boundaries without dislocations are possible in calcite. By the use of interferometric techniques, they were able to determine that the $v_n/v_s$ ratio for such a boundary is 0.06 as compared with 0.14 for a twin boundary with dislocations.

Bengus and Startsev (24), by the technique of selective etching, have shown that etch pits of two types occur at twin boundaries: the first type etches less readily than the other suggesting that the latter dislocations cause more lattice distortion than the former. Their results indicate that the first type represents twinning dislocations in that they are always displaced along the twin plane whereas the second type of etch figure is not displaced along the twin plane by external forces, but rather, they migrate together with the twin boundary in the same direction. These dislocations are found to often occur in pairs with one pit on one side of the boundary corresponding to a similar one on the other. It will be recalled that in the model of $e_1^{(+)}$ twinning presented earlier, the twinning dislocation is joined to two other partials making an obtuse angle with each other. During twinning, these partials would migrate along with the twin boundary.
4. Symmetry of Etch Figures as an Inference of the Dislocation Structure in Calcite

It has previously been mentioned that the symmetry of each etch figure appearing on a crystal face should, as a rule, conform to the symmetry elements of the point group normal to that face and that the etch pit symmetry should be one of the tem plane point groups. Figure 16a illustrates a typical etch pit pattern (etchant consists of an aqueous solution of HNO₃) on the m₁ planes in calcite. It is apparent that the dislocation lines (i.e., the lines joining the etch pits together on opposite sides of the figure) must lie normal to the two-fold axes and that an additional symmetry element consisting of a mirror plane containing the dislocation line and whose normal is parallel to the two-fold axis exists. In this particular case, it can easily be shown that the dislocations depicted are pure edge dislocations with Burgers vectors 4.99Å lying on the basal plane.

Our own studies of etch figures in calcite have shown that similar results hold when two sides of the cleavage plate are etched with a solution of HNO₃ in H₂O (1 cc HNO₃ per 100cc H₂O). By placing the etched
plate in a universal stage, it is possible to obtain a quick determination of the orientation of the dislocation line. As a rule, we found that the lines lie parallel to the \( <110> \) directions although a few lie parallel to the \( <1\overline{1}0> \) directions. The latter we believe to be screw dislocations in that the etch pits produced are asymmetric whereas those produced by the pure edge dislocations are always symmetrical. The symmetrical etch figures have been found in our experiments to greatly predominant over the asymmetric pits. In conclusion, the planes in which the dislocation lines are contained are invariably the \( f_j, \, r_i, \, m_i \) and a few have been found to lie in the \( e_i \) planes.
Part V. Suggestions for Further Work

A. Slip System Determination

The preceding investigation suggests that further study will be necessary to determine the flow mechanisms in calcite. Such an investigation should attempt to discover:

1. The active and latent slip and twin systems in calcite.

2. The temperature dependence of these systems.

3. The critical resolved shear stress (CRSS) necessary to initiate gliding and its variation with temperature.

4. The theoretical prediction of a flow curve for the calcite polycrystal based upon the determined deformation systems.

The use of high pressure apparatus, capable of sustaining high temperatures and pressures, must be employed. Determination of the gliding elements can be accomplished by the use of the following techniques:

1. The use of highly polished cylindrical cores enabling a slip line (and band) study at the conclusion of each experiment.

2. The study of etch pit movement under stress. Preliminary inves-
tigations indicate this to be a useful technique.

3. Careful application of the petrofabric techniques as developed by Turner(33).

B. Dislocation Study of Deformed Calcite

Supplementing the above work, a detailed study on the role of dislocations in the plastic flow of calcite is necessary. Some of the major problems that such an investigation should determine are as follows:

1. The critical stress required to move dislocations in the structure.

2. The mechanism of dislocation multiplication and the process involved during the multiplication of these loops so as to form glide bands.

3. The interaction of dislocations with possible obstacles as intersecting glide bands and coherent twin boundaries.

4. The properties of the unsymmetrical stacking faults resulting from dissociation of total dislocations.

5. The genesis of kink banding in calcite.
Part V. Summary

This work represents an investigation into a few of the fundamental factors known to play a dominant role in the plastic deformation of calcite and the related rhombohedral carbonates. Symmetry considerations and elementary dislocation mechanics have been utilized and both suggest that the currently accepted model of calcite deformation may be incorrect. This ambiguity can only be resolved by further experimental work, preferably with crystal orientations favoring the action of easy glide only.

Structural background has been presented in the form of a model based on a framework of $CO_3$ groups in hexagonal closest packing with the Ca ions in the octahedral interstices. Dislocation concepts have been used for interpreting the significance of the crystallographic elements of slip based on the theoretical model. The Burgers vectors of total dislocations have been discussed in terms of the crystal structure and reasons set forth suggesting that slip does not occur by a total dislocation mechanism, but rather by the movement of partial dislocations. With the aid of this model of dissociation, it has been possible to discuss the
atomic mechanism of twin gliding on $e_1$ and $r_1$ in the positive sense. The possibility of dissociation of dislocations in the Turner model has been discussed and the available evidence suggests that extended dislocations in this model are energetically unfavorable.

Recent etch pit studies of deformed calcite have been summarized and evaluated in light of the theoretical model. It was shown that these studies tend to confirm the predictions of the theoretical model.
Part VI. Appendix: Crystallographic Notation

Figures 5a and 5b represent equal-area projections (upper hemisphere) showing the poles of common faces and directions for both the calcite and NaCl structure. Rhombohedral coordinates have been utilized for important crystallographic planes and directions in the calcite lattice to facilitate its structural similarity to the NaCl-type lattice (Figure A1).

Utilizing Turner's classification (33), the following symbols allowing rapid comparison among similar planes and directions in the two structures will be used.

<table>
<thead>
<tr>
<th>CALCITE</th>
<th>HALITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_4 = c_v = (0001) = (111)$</td>
<td>$f_4 = (111)$</td>
</tr>
<tr>
<td>$f_i = {0\overline{2}21} = {1\overline{1}1}$</td>
<td>$f_i = {1\overline{1}1}$</td>
</tr>
<tr>
<td>$m_i = {10\overline{1}0} = {\overline{1}1\overline{2}}$</td>
<td>$m_i = {\overline{1}1\overline{2}}$</td>
</tr>
<tr>
<td>$r_i = {10\overline{1}1} = {100}$</td>
<td>$r_i = {100}$</td>
</tr>
<tr>
<td>$e_i = {01\overline{1}3} = {\overline{1}1\overline{3}}$</td>
<td>$e_i = {\overline{1}1\overline{0}}$</td>
</tr>
</tbody>
</table>

Individual planes are differentiated by subscript numbers—e.g.,

$r_1 = (100), r_2 = (010), r_3 = (001), \text{etc.}$

The following interfacial angles, measured between poles of planes, are useful.
Figure A1

Illustration of Rhombohedral and Cubic Crystal Axes
\[ x_1 \quad x_2 \quad x_3 \]

\[ (110) \quad (111) \]
<table>
<thead>
<tr>
<th>CALCITE</th>
<th>HALITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_4 \wedge r_1 ) = 441/2°</td>
<td>( f_4 \wedge r_1 ) = 54°</td>
</tr>
<tr>
<td>( f_4 \wedge e_1 ) = 261/4°</td>
<td>( f_4 \wedge e_1 ) = 36°</td>
</tr>
<tr>
<td>( e_1 \wedge e_2 ) = 45°</td>
<td>( e_1 \wedge e_2 ) = 90°</td>
</tr>
<tr>
<td>( e_1 \wedge r_1 ) = 703/4°</td>
<td>( e_1 \wedge r_1 ) = 64°</td>
</tr>
<tr>
<td>( r_1 \wedge r_2 ) = 75°</td>
<td>( r_1 \wedge r_2 ) = 90°</td>
</tr>
<tr>
<td>( f_1 \wedge f_2 ) = 79°</td>
<td>( f_1 \wedge f_2 ) = 64°</td>
</tr>
</tbody>
</table>
PART VIII

BIBLIOGRAPHY

   Phil. Mag., 2, 1023.
3. Bell, J.F., 1941, Morphology of mechanical twinning in crystals;
   Am. Mineralogist, 26, 1434-1452.
5. Boas, W.I., and Hargreaves, M.E., 1948, On the inhomogeneity of
   plastic deformation in a polycrystalline aggregate;
7. Cahn, R.W., 1954, Twinned crystals; Adv. in Physics, 62,
   363-445.
10. Griggs, D.T., 1936, Deformation of rocks under high confining
    pressures; Jour. Geol., 44, 541-577.


