Chapter 2

EXPERIMENTAL METHODS AND OBSERVATIONS

2.1 Precipitation in Crystalline Materials

When a solid solution at an elevated temperature is cooled slowly to room temperature or it is quench-aged at a suitable temperature extraneous phases segregate within the crystal. The second phase could be either an impurity phase rejected from the solution due to solubility limit or a decomposition product produced as a result of a solid state reaction within the crystal or between the crystal and its environment. These have been observed in several crystalline materials such as alloy systems, ceramics and semiconductors. When a non-metallic crystal is irradiated by high energy radiation or by fast particles (say, neutrons or electrons) reaction products sometimes get embedded in the crystal. All these processes which may be reversible or irreversible can be categorized in general as 'solid state precipitation'. This has been followed up by various workers by detecting changes in physical properties of the crystal, by x-ray diffraction methods or by observing the precipitate particles in an electron or optical microscope directly. Precipitation studies have mostly been directed towards understanding the mechanism and kinetics involved. These may differ from material to material. Precipitation has been described in terms of one or more of
solid state processes such as precipitation by nucleation and growth, eutectoidal or spinoidal decomposition, order-disorder, martensitic transformations, etc. These studies have also led to a basic understanding of defects in crystals because often the impurity precipitates segregate along dislocation lines.

2.2 Motivation for the Present Work

2.2.1 Various properties of alkali halides have been studied in detail over the last several decades: Ionic conductivity, thermal conductivity, dielectric loss, diffusion of indigenous or foreign point defects, optical absorption, colour centres, electron spin resonance, hardness, other mechanical properties, and so on. The interest in alkali halides is both experimental and theoretical. On the experimental side: they are easy to grow as good single crystals, they cleave, they have simple structures, they are transparent, there has always been a good scope for application, etc. The theoretical interest, starting with Born's classic work, stems from the fact that these crystals have very simple structures and that their bonding is almost entirely ionic. Both kinds of study have resulted in not only giving more information on these crystals themselves but also providing a basis for work on other materials of more or less complicated nature.

As to the effect of impurities on properties the work on these crystals has yielded particularly valuable data and ideas.
The most relevant here is the work on precipitation. As early as 1932 Rexer had observed sub-microscopic precipitate particles of a second phase (sodium metal, in fact). He could not have identified and did not identify the patterns as being due to precipitation on dislocation lines. Soon after the discovery of similar precipitation in silver halides and, what is more important, identification of dislocation patterns (Hedges and Mitchell 1953) extensive attention was paid to 'decoration' of dislocations in alkali halides. Amelinckx achieved it by means of colloidal particles of metallic sodium (1956) and also silver (Van der Vorst 1956). Mitchell and co-workers in their extensive programme on ionic crystals achieved it by diffusing gold into the crystals at high temperatures (Barber et al 1957). On the other hand, Edner (1932), Amelinckx et al (1955) and Harvey (1963) decorated dislocations by incorporating barium chloride into crystals of sodium chloride. The decorating particles of a second phase, whether metal or salt, are less than a micron in size and are just resolved in an ultramicroscope. In the photomicrographs of Harvey it is seen that some of the particles are large (~5µ) and they seem to have a discernible crystallographic shape. Amelinckx (1956) observed that, by diffusing sodium into a mixed crystal of NaCl-AgCl, silver particles segregated along dislocations in coarse networks and that a few of the precipitates had a crystallographic shape. He, therefore, supposed that the colloidal particles also have a definite crystallographic shape and orientation which could be
seen if they had been large. Since the size of precipitate particles is in general controlled by heat treatment we thought it worthwhile to investigate the conditions under which the particles grow large enough for the geometry and crystallography to be studied by direct observation in an optical microscope.

2.2.2 It was also thought worthwhile to make a systematic and detailed study of the morphology of precipitate particles and to examine the structure and energy of crystal interfaces which are generated by oriented particles with the surrounding matrix. This kind of study was considered important in the context of the renewed experimental and theoretical interest in epitaxial layers (see Chapter 5). During this analysis the question of coherency between two dissimilar ionic structures and that of the stacking of precipitate layers in relation to the matrix layers were encountered. Hence for understanding the morphology exhibited by the precipitates and also for understanding the interface structure it was essential first to identify the precipitates.

2.3 Experimental Methods

2.3.1 Optical Microscopy

The mixed crystals of NaCl-BaCl₂ were studied by several methods. Thin sections of the crystals after the intended thermal treatment were examined under a Reichert NEOZET optical microscope having useful magnifications up to
1250 X. By swinging in an auxiliary lens magnifications twice as large could be obtained but with poor resolution. By using a special kind of universal condenser called POLYPHOS (also by Reichert) a given field of view of the specimen could be successively examined under bright ground, phase contrast, anoptral contrast and dark-field illuminations. Crystals were also studied under a Reichert RCD dark field microscope which had a focusing condenser. Polarized light observations were made under an American optical POLARSTAR microscope using appropriate compensators whenever required.

Measurements on the geometry of the precipitates were made directly in the microscope using a calibrated filar micrometer eye-piece and a vernier protractor eye-piece. Measurements were also made on photomicrographs.

Photomicrographic exposures were determined by means of a Reichert REMIPHOT vacuum photocell exposure meter. For getting photomicrographs of suitable contrast ORWO 35 mm film of very low speed (6/10° Din) was used.

2.3.2 X-ray Methods

The orientations of precipitate particles in relation to matrix directions were determined by back-reflection Laue analysis. For aligning specimens a two-circle goniometer was used. In an effort to identify the precipitated phase rotating crystal photographs were taken and analysed to see if there
were any additional reflections. Debye-Scherrer photographs of samples prepared from a mixed crystal were compared with those of a pure NaCl and pure BaCl₂. The results were not encouraging probably due to weak intensity of radiation diffracted from the precipitate particles.

2.3.3 Ionic Conductivity

Thin sections of the crystal (about 5x5x1 mm) were used for measuring ionic conductivity. For good electrical contact graphite/silver paint was used on sample faces. The sample was placed between two platinum-rhodium discs held in position by four stretched springs of a conductivity cell constructed for this purpose. AC-conductivity was measured at 1kHz by using a GR impedance bridge, model 1615.

2.3.4 Micro-Hardness Testing

Micro-hardness measurements were made by means of a micro-hardness tester (model PMT-3, made in USSR) having a diamond 60°-indenter.

2.4 Precipitates in As-grown Crystals

(See published preliminary report Swamy Rao and Parasnis 1969)

Pure crystals and mixed crystals from L-batches* are

* Crystals grown from melt containing BaCl₂ in concentrations of 0.1%, 0.5% and 1% by weight will be denoted by L, M and H respectively meaning low, medium and high concentration batches.
seen to be transparent irrespective of the technique of growing (i.e. CK or HS). However, M-batch crystals looked noticeably turbid and H-batch crystals markedly so. The turbidity was greater towards the core of the as-grown crystals in the case of both CK- and HS-crystals. However, whereas it increased towards the bottom in the former it increased towards the top in the latter. Under a microscope particles of a second phase (average size: 5-60 µ) are seen precipitated throughout the interior of thin sections cleaved from M- and H-crystals. They have several different forms and crystallographic orientations (Figure 2.1). On examining cleavage sections from various parts of a crystal it is observed that the density of precipitate particles is greater wherever the turbidity also is greater. On the whole precipitates in M-crystals are more widely dispersed than those in H-crystals. When M-crystal sections are heated to an elevated temperature (\( \sim 750^\circ\text{C} \)) for 1 hr and quenched in air to room temperature the precipitates all disappear while in the case of H-crystals very fine precipitates are still observed, but only in a dark-field microscope. Oriented precipitates re-appear in crystals of either concentration when the crystals are aged at about 350°C for 12-48 hr. Precipitate size increases with ageing time. Figures 2.2(a,b,c) illustrate the precipitates formed in crystals aged at about 300°C for 6, 12, 18 hr respectively as observed in dark-field illumination. Some of the crystals were placed in a platinum filament micro-heater so that differential ageing is possible in a range of
FIGURE 2.1

(a) \{001\}_m
200X

(b) \{001\}_m
200X
FIGURE 2.2

(a) \{001\}_m 500X

(b) \{001\}_m 500X

(c) \{001\}_m 500X
temperature.* The crystal under the filament has a higher temperature as compared to regions between consecutive filaments. Figure 2.3(a, b, c) shows that the precipitates are large and widely dispersed at regions of higher ageing temperature (left hand side) than at the lower (right hand side). The three micrographs were taken in phase contrast, anoptral contrast and dark-field illuminations respectively. Some crystals were heated for 6 hr at 300°C and subsequently aged at a higher temperature (~550°C) for 6 hr. These crystals are observed to contain precipitates of the largest obtainable size (25 µ). It may be remarked that the effect of ageing temperature and time on the growth of precipitate particles depends upon the initial concentration of the impurity in the crystal. For purposes of studying the morphology of oriented precipitates any of the two samples, i.e. as-grown and slowly cooled crystals or quench-aged crystals, is suitable. However, the variety and distribution of precipitate particles are more in the case of as-grown and slowly cooled crystals** (see Figures 2.2, 2.3 in comparison to Figure 2.1).

2.5 Classification of Precipitates

The several forms of precipitate particles observed (Figure 2.1) could all be classified under two broad groups.

*We are indebted to Professor J W Mitchell, University of Virginia, for this suggestion.

**Photomicrographs should be understood to be of these specimens unless stated otherwise.
FIGURE 2.3 \{001\}_m 250X
(The 'specks' as such are excluded from this classification.)
The particles are either in the shape of long rods or polygonal platelets. All of these are crystallographically oriented in the matrix of NaCl. The platelets are in forms of hexagons, octagons, decagons, rhombi, etc. There are also other forms, viz truncated and irregular platelets. Observations were made on cleavage sections and also on sections specially cut to specific simple crystallographic orientations (§ 1.4). These are described in detail in the rest of this chapter.

2.6 Rod-like Precipitates

Two types of rods are seen when viewed along $<001>_m$.

Those of one type, denoted hereinafter as R-I, make angles of $45^\circ$ with the edges of cleavage (i.e. $\{001\}$-) sections. Figure 2.4(a, b) shows them in bright field illumination at lower and higher magnifications. Figure 2.5(a, b, c) show the same as observed along $<001>_m$ under phase contrast illumination. It is clear that the rods are oriented along $<110>_m$. By focussing the microscope at different depths it is possible to see the rods oriented along the four $<110>$-directions which are inclined to the plane of observation. The rods of the second type, denoted hereinafter as R-II, are parallel to the edges of $\{001\}$-sections; thus they are oriented along $<100>_m$ (Figure 2.6(a, b)).

*$$<uvw>_m$$ denotes a direction in the NaCl-matrix.*
FIGURE 2.5

(a) \{001\}_m
800X

(b) \{001\}_m
800X

(c) \{001\}_m
2000X
FIGURE 2.6

(a) \{001\}_m

800x

(b) \{001\}_m

2000x
The lengths of R-I are typically in the range of 15-30 µ. The lengths of R-II show a wider variation, 5-20µ, but on the whole they are shorter and far less numerous than R-I. There are also rods which are off-<110>_m and off-<100>_m orientations. These are seen in Figure 2.7 wherein they have together with R-I and R-II decorated sub-boundaries in the crystal. Some of them are also seen at isolated sites. But these are not as predominant as R-I and R-II. R-I rods are colourless whereas the straight central part of R-II rods looks reddish in colour surrounded by a pale-greenish hue enclosing the contour (Figure 2.6(a,b) being photomicrographs in black and white the coloured appearance of R-II is not seen). This is very probably a purely optical effect. Viewed along <110>_m, one orientation of R-I is focussable in the plane of observation and four others can be followed in depth. The sixth rod is seen as a 'speck' which can be followed in depth (≈ 10-15µ). Similarly, on a given (110)-plane one orientation of R-II is expected to be seen in the plane of observation. It is found that such a 'rod' is in fact merely an edge (parallel to <110>_m) of a platelet lying at 45° to the plane of observation, i.e. parallel to a (100)-plane. When observations are made along <111>_m three different orientations of R-I making angles of 60° with one another are seen. Laue analysis confirmed that they are oriented along <110>_m. Figure 2.8a shows a number of rods viewed at low magnification along a <111>_m-direction. Figure 2.8(b,c) are photomicrographs taken at higher magnifications. In these
FIGURE 2.7

(a) \{001\}_m
400X

(b) \{001\}_m
800X
FIGURE 2.8

(a) \{111\}_m \ 200X

(b) \{111\}_m \ 800X

(c) \{111\}_m \ 800X
there are very long and pointed rods (\( \sim 50-70 \mu \)) which also are oriented along \(<110>_m\). These seem to be some other kind of rods which are not observed as rods on \(\{001\}_m\) and may therefore be denoted as R-III. These are greenish and reddish in colour all along. Further careful observations show that R-II and R-III are not true R-I (i.e., R-I can be observed along \(<001>_m\), \(<110>_m\) and \(<111>_m\)-directions, but it is not so in the case of R-II and R-III). In Figure 2.8b there is one R-I and two R-III (cf. Figure 2.5).

2.7 **Polygonal Platelets**

Of the several forms of platelets observed the predominant forms are hexagons, octagons, decagons and parallelograms. (Some of the parallelograms are rhombi.) There are many other forms also which are not as numerous as these. They are only truncated or less regular forms of the above basic ideal forms.

2.7.1 **Hexagons**

There are two types of hexagonal platelets. One type are more or less regular while the other type are narrow and elongated. Figure 2.9(a,b,c) are photomicrographs taken on a cleavage section showing these platelets. The same area as in 2.9a is shown at a higher magnification in Figure 2.9c. The first type

\[
\{hkl\}_m
\]
denotes a plane in the NaCl-matrix.
are henceforth designated as H-I and the other as H-II. Both
are seen in the photomicrograph taken in phase contrast illu-
mination in Figure 2.9b. H-I is at the left and H-II at the
right. Figure 2.10(a,b) shows H-I at lower and highest magni-
fications in phase contrast illumination. Figure 2.11a and
Figure 2.11b show H-I and H-II respectively in dark-field
illumination (see also Figure 2.19c). H-I and H-II have their
sizes in the ranges 10-25µ and 10-60µ respectively. Viewed
along <100>\textsubscript{m}, platelets of type H-I look as though they are
slightly stretched along either a diagonal or a line joining the
centres of opposite sides (Figure 2.10b). It is seen that there
are several orientations (see Figures 2.9, 2.10). It is also
seen that none of the sides of any of the H-I platelets is
contained in the plane of observation. In Figure 2.12a a vertex
of an H-I is focussed sharp at high magnification and an opposite
vertex of the same platelet at a depth of 10µ is focussed in
Figure 2.12b. Thus the platelets are parallel to planes inclined
to \{001\}_\textsubscript{m}. The hexagonal symmetry of these platelets and the
various aspects of their orientation are consistent with the
expectation that they are parallel to \{111\}_\textsubscript{m}. On the other hand,
only two orientations of H-II platelets are observed when viewed
along <100>\textsubscript{m} and their long dimensions are mutually perpendicular
(Figure 2.1a at middle left). Their long sides are parallel to
<110>\textsubscript{m} (Figure 2.9b; also 2.23b). It is clearly seen in
Figure 2.11b (also 2.19c) that an H-II is composed of two platelets
lying parallel to two different \{hkl\}_\textsubscript{L}-planes whose common section,
FIGURE 2.10

(a) $\{001\}_m$ 500X

(b) $\{001\}_m$ 2000X
FIGURE 2.11

(a) \(\{001\}_m\)

500X

(b) \(\{001\}_m\)

1500X
FIGURE 2.12 \{001\}_m 1500X
seen as a distinct line, being parallel to the two long sides is parallel to $<110>_m$. In Figure 2.13 an H-II platelet is focussed successively in depth along $<110>_m$ (a=some depth, b=3μ lower, c=another 3μ lower). The line joining the pointed ends is barely visible in Figure 2.13b whereas it is resolved quite clearly under dark-field illumination in Figure 2.11b. The largest (60μ) H-II seen is shown in Figure 2.14a, with its central straight 'bend' clearly resolved under phase contrast illumination. Figure 2.14b shows an H-II that has disintegrated into small particles which are still in situ. The cause of disintegration could be any or all of the following: the H-II platelets are incoherent precipitates; there has been severe damage after complete growth; the growth itself is incomplete etc. Figure 2.14c shows some fine markings which appeared on H-I and H-II in the neighbourhood of a cleavage crack in one specimen.

On viewing along $<110>_m$ some of the H-I platelets appear (but are not) somewhat regular (Figure 2.15) as compared to their irregular appearance when viewed along $<100>_m$ (cf Figures 2.9, 2.10). None of the sides is contained in $\{011\}_m$. Only one orientation of H-II can be seen when followed similarly to Figure 2.12.

As expected, H-I platelets are regular when viewed along $<111>_m$(Figure 2.16(a,b,c)). In other words, their planes are in fact parallel to $\{111\}_m$. Their sides and vertices are sharp.
FIGURE 2.13 \{001\}_m 1500X
FIGURE 2.14

(a) \{001\}_m 2000X

(b) \{001\}_m 2000X

(c) \{001\}_m 1500X
FIGURE 2.15 \{(110)\}_{m} 500x
FIGURE 2.16

(a) \(\{111\}_m\) 500X

(b) \(\{111\}_m\) 800X

(c) \(\{111\}_m\) 800X
The angles between adjacent sides are 120°. On a given (111)\textsubscript{m} there are two orientations as seen in Figure 2.17(a,b) and Figure 2.18(a,b,c). It is seen that the hexagonal platelet in one orientation is rotated with respect to the other by about 22°. By back-reflection Laue analysis it is established that the sides of a hexagon are parallel to one of two possible sets of <123>\textsubscript{m}. It is thus understandable that H-I platelets when viewed along <100>\textsubscript{m} could be sorted out into four groups of two orientations each. (Slight irregularities in photomicrographs are due to crystal-grinding and photographing errors.)

The interpretation of the morphology of these platelets given in Chapter 5 is based entirely on the important observation that the sides of H-I platelets are all parallel to <123>\textsubscript{m}. Three orientations of H-II platelets are observed when viewed along <111>\textsubscript{m} two of which are seen in Figure 2.16a. The line joining the pointed ends is parallel to <110>\textsubscript{m}. The density of H-II platelets is on the whole less than that of H-I platelets, the latter being about $10^4$ cm$^{-2}$.

2.7.2 Octagons

The next predominant form of platelets is the octagons (size: 10-25 µ) which are of two types. Figure 2.19(a,b) shows four different orientations of octagons lying parallel to some planes, (hkl)\textsubscript{m}, inclined to the plane of observation, viz to (001)\textsubscript{m}. (See Figure 2.5b also.) These appear to be irregular but may very well be regular in their respective planes.
FIGURE 2.17

(a) $\{111\}_m$
800X

(b) $\{111\}_m$
1500X
FIGURE 2.18
They will henceforth be denoted as 0-I. Figure 2.19(c,d) shows 0-I platelets viewed along <001> under dark-field illumination. In Figure 2.19c an H-II platelet is seen to which a reference was made earlier. Figure 2.19(e,f) shows an 0-I at the highest magnification (Figure 2.19e: some depth, Figure 2.19f: 9µ below).

The other type, denoted as 0-II, is illustrated in Figure 2.20(a,b,c). (See also Figure 2.16.) There are two orientations on a given (001)_{m}-plane which seem to be obtained by the truncation of a rectangle (with sides parallel to [100]_{m} and [010]_{m}) at its four corners. The new sides thus formed are usually all equal, opposite sides being parallel. In Figure 2.20b the truncation at the adjacent corners at the left is greater than that at the other two. The new sides of platelets in the two orientations are parallel to <210>_{m} and <120>_{m} respectively. In some of the platelets straight bands parallel to the breadth are observed as shown in Figure 2.20c. This has been observed invariably in platelets lying in the vicinity of cleavage cracks in a crystal (cf Figure 2.14c). On the whole, 0-II platelets are far less numerous than 0-I platelets. Although it is not possible easily to distinguish 0-I and 0-II from each other when viewed along <110>_{m} (since both are inclined) they can easily be distinguished when viewed along <111>_{m} (see Figure 2.21).

On a given (111)_{m} an 0-I platelet can be in one of three possible orientations. Figure 2.22(a,b) and 2.27g show 0-I
FIGURE 2.19

(c) \{002\}_m
800X

(d) \{001\}_m
2000X
FIGURE 2.21 \( \{110\}_m \) 2000X
oriented on a (111)_m-plane. This platelet is essentially a semi-regular octagon with its opposite sides equal and parallel. In a fully grown platelet the alternate sides are of equal length and the angles are alternatively 120°. The remaining four angles are alternately about 142° and 158°. The eight sides of a given 0-I platelet include two directions from each set of <123>_m; in other words, one <123>_m from each set is missing in any given 0-I platelet. The morphology of 0-I-platelets is quite interesting and is discussed in Chapter 5 (see Figures 5.1 and 5.3).

2.7.3 Decagons

Platelets observed in the shape of a decagon (henceforth referred to as D) are of only one type but in several orientations. They are about as numerous as 0-I octagons but their size is larger (average ~25 µ). Figure 2.23a shows a decagon in one orientation observed under bright field illumination. Decagons in three different orientations are shown in Figure 2.23b. Figure 2.23c shows a decagonal platelet at the highest magnification under phase contrast illumination. In Figure 2.24(a,b,c) a decagonal platelet is viewed along <100>_m, focussed successively lower in depth at intervals of 4µ and 5µ. Figure 2.24(d,e,f) is another area in the same crystal showing decagons in two orientations focussed successively lower in depth.

Thus these platelets are, like H-I and O-I, inclined to {001}_m and have none of their sides parallel to a direction lying in {001}_m- and {110}_m-planes. Figure 2.25(a,b) shows decagons at lower and
FIGURE 2.24 \(\{001\}_m\) 1500X
FIGURE 2.24 \{001\}_m 1500X
FIGURE 2.25

(a) \{\{111\}_m\}

500X

(b) \{\{111\}_m\}

800X
higher magnifications as seen along \(<111>_<m>\). The two decagons of Figure 2.25 are in different orientations on the same \((111)_m\). Clearly the decagonal platelets lie parallel to \([111]_m\). After studying them in a number of \([111]_m\)-sections it was clear that there are six different orientations on a given \((111)_m\). The sides of a given platelet include all but one of the six \(<123>_m\).

Accordingly, there can be six different orientations only, as observed. (Vide Figures 5.1 and 5.4 in Chapter 5, and the discussion therein.)

Figure 2.26 shows the orientations of the forms H-I, O-I and D on a standard \((111)_m\) stereographic projection. Only one orientation each of O-I and D is shown so as not to complicate the diagram.

2.7.4 Platelets of Other Shapes

There are several other forms of platelets most of which are either in the form of rhombi or parallelograms (size: 5-20 \(\mu\)). Observations made along \(<100>_m\) and \(<110>_m\) show that none of their sides is parallel to directions lying in \([001]_m\) and/or \([110]_m\) (see Figure 2.10b). Viewed along \(<111>_m\), it is clear that the platelet planes are parallel to \([111]_m\). Their adjacent sides are parallel to \(<123>_m\)-directions, being any two from among the six. Figure 2.27(a,b) shows parallelograms in two different orientations on a \((111)_m\)-plane. In addition to these, other shapes are also encountered but they are not as predominant. For instance, Figure 2.27(c,d,e,f,g) shows platelets
Fig 2.26  Stereographic projection of \((111)_m\) showing the relative orientations of different platelet forms.
(c) \{001\}_m
500x

(d) \{001\}_m
500x

(e) \{001\}_m
800x

FIGURE 2.27
FIGURE 2.27

(f) \{001\}_m
1500X

(g) \{111\}_m
800X
with re-entrant corners. Of these, only $g$ is the view along $\langle 111 \rangle_m$; the others are along $\langle 100 \rangle_m$. $d$ and $e$ show the same platelets in different illuminations.

2.8 Polarized Light Observations

All of the oriented precipitates were examined between crossed polaroids in a polarizing microscope in order to obtain optical information about the nature of their material. It was also thought desirable to see if the precipitates had introduced any strain in the surrounding matrix. When the sample on the stage of the microscope was rotated while viewing the precipitates between crossed polaroids there was no detectable birefringence in the immediate vicinity of a precipitate. This was confirmed by inserting a full-wave retardation plate of first order red (which is a more sensitive test).

2.8.1 Rod-like Precipitates

Viewed along $\langle 001 \rangle_m$ under crossed polaroids, R-I rods are extinct for any orientation of the specimen while for an arbitrary orientation of the specimen R-II rods are not. Figure 2.28a shows some R-II rods and one R-I rod viewed along $\langle 001 \rangle_m$ by transmitted light. Figure 2.28b shows the same area viewed between crossed polaroids. It is seen that R-I is extinct while R-II are not. It may be concluded that rods R-I and R-II are made of two different materials, the former being cubic and the latter non-cubic. In order to find whether
FIGURE 2.28

(a) \{001\}_m
800X

(b) \{001\}_m
800X
they are made of the same material and/or their optical orientations are different, observations were made along $<110>_m$ and $<111>_m$. The observation was confirmed. Similarly, R-III rods are also found to be non-cubic. Both R-II and R-III show direct extinctions. The optical character of these rods was investigated by making use of retardation plates. The following results were obtained. (S and L denote 'slow direction' of the retardation plate and 'length' of the rod respectively.)

<table>
<thead>
<tr>
<th>Compensator</th>
<th>R-II</th>
<th>R-III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S \parallel L$</td>
<td>$S \parallel L$</td>
</tr>
<tr>
<td>(a) $\lambda$-plate, Gypsum</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>(b) $\frac{1}{4}$-plate, Mica</td>
<td>Original colour</td>
<td>Grey</td>
</tr>
<tr>
<td>(c) Quartz Wedge</td>
<td>Compensated</td>
<td>Compensated</td>
</tr>
</tbody>
</table>

In either type of rods the red band sweeps the field of view just after the compensation. It was observed that rods R-II and R-III show green and blue interference colours of the first order respectively. It is also observed that their slow direction is parallel to their length and that they have positive sign of optical elongation. All this evidence is not sufficient to find out exactly whether they have uniaxial or biaxial character. However, it is thought that they have an orthorhombic structure.
2.8.2 Polygonal Platelets

H-I platelets do not show any birefringence although this is somewhat difficult to see because of a good deal of scattered light. Observations along \( <110> \text{m} \) and \( <111> \text{m} \) confirm that they are made of cubic material. H-I platelets in either orientation remain extinct for any arbitrary orientation. Similar results are obtained in the case of O-I platelets, decagons, rhombi/parallelograms, etc showing thereby that they all are made of cubic material.

As regards non-cubic platelets, viz H-II and O-II, it is observed that when they are viewed along \( <001> \text{m} \) only two of their orientations are extinct. This means that one of their optic axes is directed parallel to \( <001> \text{m} \). On the other hand, when H-II platelets are viewed along \( <111> \text{m} \) only three orientations remain extinct. Thus the other optic axis of H-II may be parallel to \( <111> \text{m} \). However, it was not possible to make observations on O-II along \( <111> \text{m} \) as it was difficult to make cut O-II platelets. These limited observations suggest that if H-II and O-II platelets are of identical material then their optic axes are parallel to \( <001> \text{m} \) and \( <111> \text{m} \) respectively. However, they are not conclusive.

2.9 Summary of Microscopic Observations

The observations described above are summarized in Table 2.1, and all precipitate forms shown schematically in
<table>
<thead>
<tr>
<th>Oriented precipitates</th>
<th>Size (microns)</th>
<th>Density per cm²</th>
<th>Number of Distinct orientations</th>
<th>Orientation w.r.t. matrix Plane</th>
<th>Directions</th>
<th>Nature of precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-I</td>
<td>15-30</td>
<td>$2.5 \times 10^5$</td>
<td>6</td>
<td>-</td>
<td>$&lt;110&gt;$</td>
<td>Cubic</td>
</tr>
<tr>
<td>R-II</td>
<td>5-20</td>
<td>$3 \times 10^3$</td>
<td>3</td>
<td>-</td>
<td>$&lt;100&gt;$</td>
<td>Non-cubic</td>
</tr>
<tr>
<td>R-III</td>
<td>20-70</td>
<td>$8 \times 10^4$</td>
<td>6</td>
<td>-</td>
<td>$&lt;110&gt;$</td>
<td>Non-cubic</td>
</tr>
<tr>
<td>H-I</td>
<td>10-25</td>
<td>$1 \times 10^6$</td>
<td>8</td>
<td>${111}$</td>
<td>$&lt;12\overline{3}&gt;$ or $&lt;21\overline{3}&gt;$</td>
<td>Cubic</td>
</tr>
<tr>
<td>H-II</td>
<td>10-60</td>
<td>$8.9 \times 10^4$</td>
<td>6</td>
<td>${hk1}$</td>
<td>$&lt;110&gt;$ &amp; $&lt;210&gt;$</td>
<td>Non-cubic</td>
</tr>
<tr>
<td>O-I</td>
<td>10-25</td>
<td>$3.5 \times 10^5$</td>
<td>12*</td>
<td>${111}$</td>
<td>$&lt;12\overline{3}&gt;$ &amp; $&lt;21\overline{3}&gt;$</td>
<td>Cubic</td>
</tr>
<tr>
<td>O-II</td>
<td>10-20</td>
<td>$5 \times 10^3$</td>
<td>3*</td>
<td>${001}$</td>
<td>$&lt;100&gt;$ &amp; $&lt;210&gt;$</td>
<td>Non-cubic</td>
</tr>
<tr>
<td>D</td>
<td>15-25</td>
<td>$1.6 \times 10^5$</td>
<td>24</td>
<td>${111}$</td>
<td>$&lt;12\overline{3}&gt;$ &amp; $&lt;21\overline{3}&gt;$</td>
<td>Cubic</td>
</tr>
<tr>
<td>Rh/P</td>
<td>5-20</td>
<td>$4 \times 10^4$</td>
<td>Several</td>
<td>${111}$</td>
<td>$&lt;12\overline{3}&gt;$ &amp; $&lt;21\overline{3}&gt;$</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

* Equivalent orientations in the same plane are not counted. (See Figure 5.3.)
Figure 2.29. A few remarks may be made on the forms shown in this figure. One, although the 'rod' R-III is shown as having pointed ends which are symmetrical, in actual fact the ends are bound to be unsymmetrical as seen in Figure 2.8c, when seen along $\langle 111 \rangle_m$. Two, the form with re-entrant corners could be $P'$ (i.e. one derived from $P$) as well as $Rb'$ although only the latter has been shown. Three, the rounded ends of R-II are, as remarked earlier, a purely optical effect. An appropriate geometrical section of O-II (which R-II is) should show flat ends (say, when a cardboard model is sectioned). Four, among all these forms H-II (hence R-III) is the only one that is dihedral.

2.10 Chemical Test and Etching

Crystals containing oriented precipitates were dissolved completely in distilled water. When the solution was tested with dilute sulphuric acid a milky-white substance precipitated. This was confirmed to be barium sulphate. This chemical test shows that the oriented precipitates are barium chloride.

Cleavage sections were etched in glacial acetic acid containing ferric ions (Barber 1969). Around the oriented platelets there was no special etch pit pattern. However, it was difficult to make out whether or not there was any special pattern around rods.
Fig 2.29 Schematic diagram showing the various forms of oriented precipitates
2.11 Ionic Conductivity

The specific conductivity of crystals containing oriented precipitates was measured at 100°C, 300°C and 600°C. The conductivity of air-quenched crystals in which precipitates had been dissolved by heating to an elevated temperature (~ 780°C) was also measured. It was found that the conductivity of the latter was higher by an order of magnitude than that of the former. The conductivity of quenched crystals (i.e., solution-treated) decreased with time on ageing. When these samples were examined in the microscope they were observed to contain oriented precipitates. This demonstrates that the conductivity of a crystal is higher when the impurity precipitates are in solution and lower when the impurity precipitates out of the solid solution. Since such measurements have become standard, it is not thought worth while to reproduce (1/T-log σ) curves here.

2.12 Micro-Hardness Testing

The following are the DPH numbers (in Kg mm⁻²) measured on various samples:

<table>
<thead>
<tr>
<th>Crystal sample</th>
<th>DPH number</th>
<th>Percentage increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) NaCl, (BDH 'Analar', annealed)</td>
<td>14.71±0.02</td>
<td>-</td>
</tr>
<tr>
<td>(b) NaCl, containing BaCl₂-platelets</td>
<td>15.26±0.02</td>
<td>3.74</td>
</tr>
<tr>
<td>(c) NaCl, platelets in solution, i.e. quenched from 750°C</td>
<td>16.70±0.02</td>
<td>13.53</td>
</tr>
<tr>
<td>(d) NaCl, containing R-I, R-II &amp; R-III</td>
<td>22.33±0.02</td>
<td>51.81</td>
</tr>
<tr>
<td>(e) NaCl, containing small rods</td>
<td>28.54±0.02</td>
<td>94.04</td>
</tr>
</tbody>
</table>

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