PART-I

GENERAL INFORMATION ON AMMONIUM HYDROGEN d-TARTRATE

EXPERIMENTAL TECHNIQUES

ERROR ANALYSIS

GROWTH AND DISSOLUTION OF CRYSTALS

CHAPTER - 1

GENERAL INFORMATION ON AMMONIUM HYDROGEN d-TARTRATE

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1.1 INTRODUCTION

Ammonium-hydrogen-d-tartrate (d-AHT) is a piezoclectric crystal.[1,2] (Zalina and Ersova, 1958 ; Mason, 1950). In literature, some information is available regarding its structure and composition. Its piezoelectric and other properties are not studied in detail. The growth of crystals was carried out by solution method. General information available so far is presented here. The crystal will henceforth be referred to as d-AHT.

1.2 PREPARATION

d-AHT is usually prepared in laboratory by producing a chemical reaction of ammonium hydroxide with tartaric acid.[3] (Howley, 1971).

The single crystals of d-AHT were obtained by preparing saturated solution at higher temperature (50°C) and gradually cooling the solution of this salt. The crystals were small in size. The solubility of d-AHT in distilled water is 3.24 g/100 cc. at 25°C.[4,5] (Clifford, 1964 ; Weast, 1964). Its chemical formula is reported in the literature as NH_4.H tartrate,[6] (Bommel and Bijvoet, 1958) $NH_4HC_4H_4O_6$

(ammonium acid D-tartrate)^9 (Wyckoff, 1951), $C_4H_4NH_6^7$, $C_4H_4O_6(NH_4).H^{13}$ (Lasheen, 1964) (ammonium hydrogen d-tartrate) NH_4-H tartrate belongs to isomorphic series of hydrogen tartrates such as : RbH, KH and C_5H tartrates. Tartrate crystals show many interesting physical properties such as ferroelectric~~s~~, piezoelectric~~s~~ etc. The group of acidic tartrates in general possesses low solubilities and is not available in nature.

1.3 CRYSTAL STRUCTURE

The crystal structure of d-AHT was analysed by x-rays^6 (Bommel and Bijøvoet, 1958). The crystals are orthorhombic with $a = 7.648 A^o$, $b = 11.066 A^o$ and $C = 7.843 A^o$; space group $P_{2_1 2_1 2_1}$; 4 molecules per unit cell (Z = 4). The atomic co-ordinates and anisotropic temperature factor parameters were calculated by method of least-squares and from three dimensional difference Fourier maps. Figures 1.1(a) and (b) show the electron density of d-AHT projected on {100} and on {001} , respectively. The Fourier maps showed a considerable overlap. To find out accurate co-ordinates, a three-dimensional analysis was carried out. Later on a structural refinement of $C_4H_9NO_6$ has been completed from data obtained on

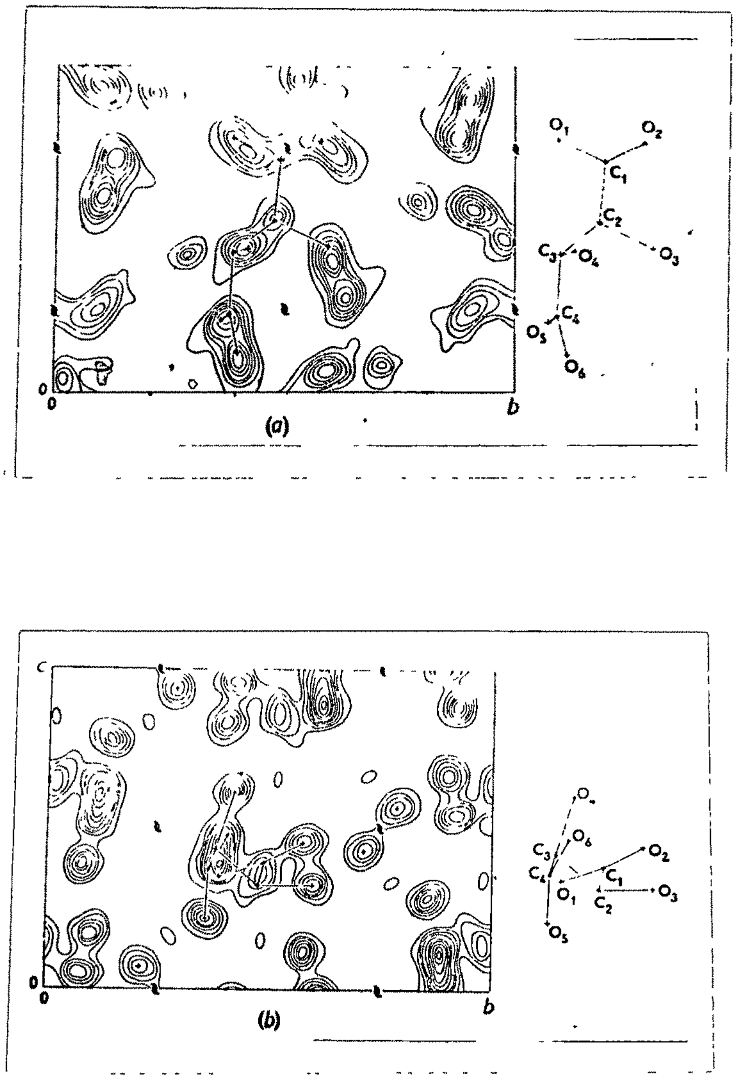

Fig. 1.1 Electron density of NH_4-H-tartrate projected (a) on (100) (b) on (001) Contours are drawn at equal intervals on an arbitrary scale.

an Enraf Nonius CAD-4 x-ray diffractometer equipped with a Si(Li) solid-state detector.[7] (Mullica et al. 1979). Tables 1.1, 1.2 represent data on band distances and angles. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms, except H_1 and H_2, were refined isotropically.

The crystals are elongated prisms in the [100] direction, and belong to the orthorhombic disphenoidal crystal class[8] (Groth, ~~1906~~-19). The bond lengths and angles of tartrate anion in d-AHT are schematically shown in fig. 1.2. Fig. 1.3 represents the orthorhombic structure of d-AHT projected along its C_o axis (Right-hand axes) and packing drawing along its C_o - axis, respectively. The large black circles are ammonium, the smaller ones are carbon atoms whereas the larger oxygen atoms are dot and short line shaded.[9] (Wyckoff, 1951). As in the crystal structures of all tartrates, here too the carbon chain and the oxygen and carbon atoms of each half CHOH-COOH of the tartaric acid molecule are nearly planar.[10-12] (Beevers & Hughes, 1941 ; Stern & Beevers, 1950 ; Sprenkels, 1956). From the intermolecular band lengths and angles, it is clear

Table 1.1

Bond distances (A°) and angles (°) of d-AHT

Bond	A(A°)	Angle	A(°)
$C_1 - O_1$	1.306(4)	$O_1-C_1-O_2$	124.7(3)
O_2	1.213(4)	$O_1-C_1-C_2$	112.1(3)
C_2	1.527(4)	$O_2-C_1-C_2$	123.2(3)
		$C_1-C_2-C_3$	110.4(3)
$C_2 - O_3$	1.421(4)	$C_1-C_2-O_3$	109.3(3)
C_3	1.526(4)	$C_3-C_2-O_3$	110.0(3)
H_1	1.03 (3)	$H_1-C_2-C_1$	105.0(18)
		$H_1-C_2-C_3$	113.6(16)
$C_3 - O_4$	1.411(4)	$H_1-C_2-O_3$	108.5(18)
C_4	1.536(4)	$O_5-C_4-O_6$	125.0(3)
	1.06 (3)	$C_3-C_4-O_5$	117.0(3)
		$C_3-C_4-O_6$	118.0(3)
$C_4 - O_5$	1.255(4)	$C_2-C_3-C_4$	108.5(3)
O_6	1.260(4)	$C_2-C_3-O_4$	111.7(3)
		$C_4-C_3-O_4$	113.3(3)
$O_1 - O_6$	2.560(3)	$H_2-C_3-C_4$	109.4(20)
H_5	0.85 (4)	$H_2-C_3-C_2$	105.1(19)
		$H_2-C_3-O_4$	108.5(19)

cont....

Table 1.1 cont...

O_3 - O_6	2.741(3)	H_3-O_3-C_2	105.4(27)
H_3	0.95(5)	H_4-O_4-C_3	111.6(32)
		H_5-O_1-C_1	112.0(32)
O_4 - O_5	2.810(4)	C_4-O_5-H_4	102(1)
H_4	0.82 (3)	C_4-O_6-H_3	135(1)
		C_4-O_6-H_5	114(1)
O_5 - H_4	2.00 (4)	O_3-H_3-O_6	164(4)
		O_4-H_4-O_5	170(4)
O_6 - H_3	1.82 (5)	O_1-H_5-O_6	169(4)
H_5	1.72 (4)	H_6-N-H_7	121(6)
		H_6-N -H_8	93(5)
N - H_6	0.87 (7)	H_6-N -H_9	99(7)
H_7	0.76 (6)	H_7-N -H_8	112(5)
H_8	0.86 (7)	H_7-N -H_9	111(6)
H_9	0.84 (8)	H_8-N -H_9	118(6)

Table 1.2

Nitrogen-oxygen distances

N - O_1	I	3.13_4 A°
N - O_5	I	2.96_7
N - O_2	II	2.85_5
N - O_3	II	3.08_9
N - O_4	III	2.88_8
N - O_5	III	2.90_9
N - O_2	IV	2.87_9
N - O_3	IV	3.15_5

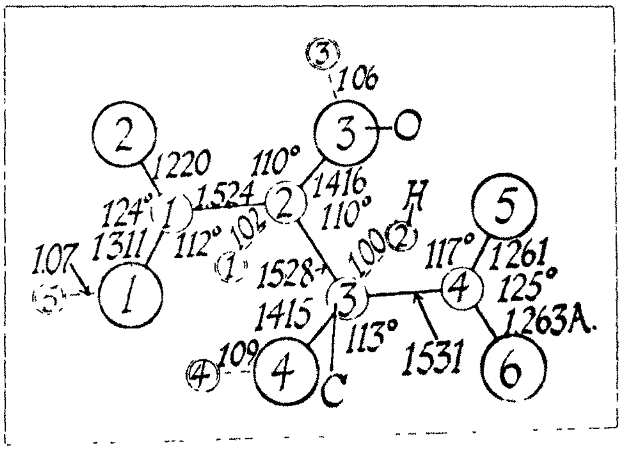

Fig. 1.2 Bond dimensions in the tartrate anion in $NH_4HC_4H_4O_6$

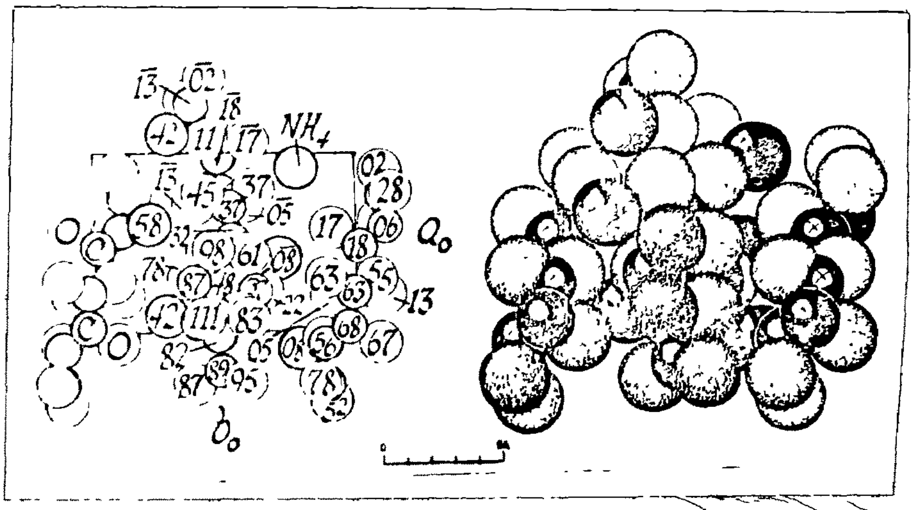

Fig. 1.3(a) (left) The orthorhombic structure of $NH_4HC_4H_4O_6$ projected along its C_o axis. Right-hand axes.

(b) (right) A packing drawing of the orthorhombic $NH_4HC_4H_4O_6$ arrangement seen along its C_o axis. The larger black circles are ammonium, the smaller ones carbon. The larger oxygen atoms are dot-and short-line shaded.

that the two halves of the molecule in respect to the carboxyl groups are different. The euquality of the C(4) - O(6) and C(4) - O(5) distances in contrast to the different distances of the oxygen atoms from C(1) suggests that the former is the ionized part of the anion.

The crystal structure of d-AHT consists of layers perpendicular to the [010] direction. Layers of hydrogen bonded tartrate ions are separated by layers of cations (Fig. 1.4).

Each NH_4^+ ion is surrounded by eight oxygen atoms in a deformed cubic environment. The distances N-O are given in Table 1.3. The hydrogen bonds of one tartaric ion with its surrounding within the layer are shown in Fig. 1.5. Of the non-symmetrical carboxyl-group $C_1O_1O_2$ the atom O_1 has a distance of $2.55A^o$ to the atom O_6 of the next ion. The distance O_1-H_5 is $1.07A^o$.

The other hydrogen bonds are between the atoms $O_3^{I} - O_6^{II}$ and $O_4^{I} - O_5^{II}$ (molecule II arises from I by the operation of the two fold screw axis [001]):

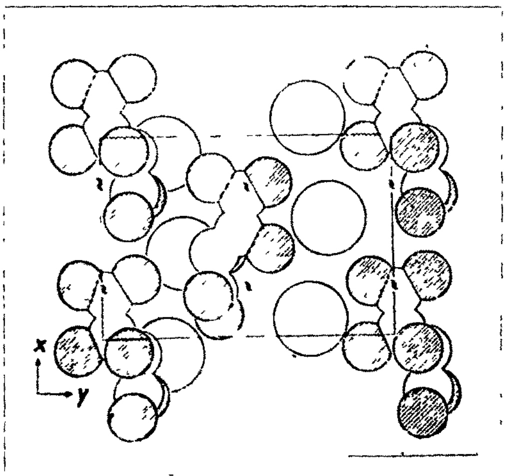

Fig. 1.4 The [001] projection of the cell content between $Z = 0$ and $Z = 1/2$. The whole projection can be found by the operation of the screw axes [001].

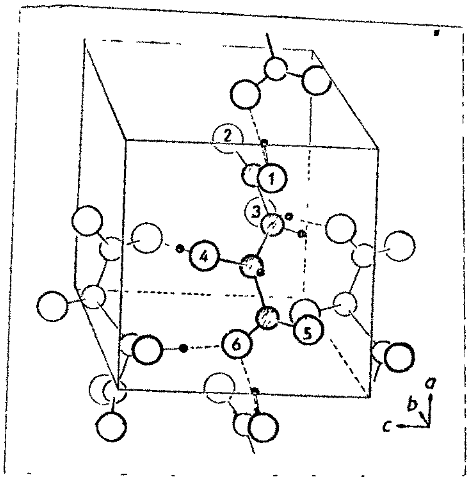

Fig. 1.5 Hydrogen bridges between a tartrate ion and its surroundings

$O_3^{I} - O_6^{II} = 2.74A^o$, $O_3 - H_3 = 1.06A^o$

$O_4^{I} - O_5^{II} = 2.80A^o$, $O_4 - H_4 = 1.09A^o$

In all three cases, the hydrogen atoms lie near the line connecting the bonded oxygen atoms.

1.5 PROPERTIES AND USES

The d-AHT crystals exhibit diamagnetic anisotropy[13] (Lasheen, 1964). The molecular susceptibilities and anisotropy are related to the molecular shape and constitution, and to the bond character, which in general markedly decreases the anisotropy. This decrease varies not only with the nature of the substituents but with their positions on the nucleus. The Krishnan-Banerjee (1935)[14] method was used in the determination of the magnetic anisotropy of the crystal. Susceptibility measurements were also carried out by Joussot - Dubien et al.[15](1956)

The crystal is weak piezoelectric, but the detail study about this property is not available in literature. Mason (1950)[1] measured the electromechanical coupling which was obtained to be strong (8% to 30% or higher). Table 1.3 briefly reports the physical properties of d-AHT.

This material possesses low toxicity and is useful for baking powder[3] (Howley, 1971). Its potentiality as a piezoelectric crystal is not yet fully explored.

The present work reports in detail systematic study of growth, dissolution and microhardness of gel-grown synthetic single crystals of ammonium-hydrogen-d-tartrate. The report is given in different parts of the present work.

Table 1.3

Information about some physical properties of d-AHT

(i)	Molecular weight	167.12
(ii)	Colour	Colourless
(iii)	Specific gravity	1.636
(iv)	Melting point	decomposes before melting
(v)	Solubility in 100 ml of distilled water	2.35 g at 15°C 3.24 g at 25°C
(vi)	Crystal structure :	
	(a) System	Orthorhombic
	(b) Class	Sphenoidal (orthorhombic disphenoidal)
	(c) Space group	$P_{2_1 2_1 2_1}$
	(d) Lattice parameters	a = 7.648 A^{O} b = 11.066 A^{O} c = 7.843 A^{O}
	(e) Number of molecules in unit cell	Z_4
(vii)	Habits (Observed by the present author)	a) Needle shape b) orthorhombic disphenoidal c) Sphenoidal
(viii)	Electromechanical property	Weak piezoelectric Material, Electro-mechanical coupling 8 to 30%
(ix)	Magnetic Property	Exhibits Diamagnetic anisotropy

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1.1 Electron density of NH_4-H-tartrate projected (a) on (100) (b) on (001). Contours are drawn at equal intervals on an arbitrary scale

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1.4 The [001] projection of the cell content between Z = 0 and Z = 1/2. The whole projection can be found by the operation of the screw axes [001].

1.5 Hydrogen bridges between a tartrate ion and its surroundings.

CHAPTER - 2

EXPERIMENTAL TECHNIQUES

* * *

2.1 INTRODUCTION

The various experimental techniques employed during the course of this work are briefly described here. For growing single crystals of ammonium-hydrogen-d-tartrate, a gel method was used. Different methods to prepare solution are given here. To grow crystals at constant temperature, the test tubes containing solutions were kept in an oven or incubator. The detailed method of growing d-AHT is given in part - II. X-ray diffraction technique was used for characterisation of crystal and optical study was carried out for quantitative and qualitative measurements of features on crystal surfaces. Etch method was used to assess the imperfect nature of d-AHT. The static indentation technique was employed to carry out microhardness studies of d-AHT. The diamond pyramidal indenters were used with Carl Zeiss VERTIVAL microscope. Excellent accounts are available on optical microscopy. (e.g. see Thompson, 1954)[1], on indentation techniques (e.g. see Mott, 1956)[2], on crystal growth in gel[3] (Henisch, 1970) and on etch phenomena on crystalline surfaces.[4] (Cabrera and Vermilyen, 1958).

2.2 PREPARATION OF A SOLUTION

It is customary to express composition of a solution in the following ways :

(i) Percentage by Volume

Suppose X c.c. of a solution A is poured in Y c.c. of solution B such that $X + Y = 100$, then X and Y express the percentages of the concerned solutions. e.g. If 20 c.c. of tartaric acid solution is poured into 80 c.c. of sodium metasilicate solution, tartaric acid solution in the mixture is 20%.

(2) Molarity

The number of gram molecules of a solute dissolved in one litre of the solution is called Molarity of the solution. This is also called molar concentration or molar strength, Suppose that X grams of solute of molecular weight W are dissolved in total volume of Y liter~~es~~, then the molarity M of solution will be

$$M = \frac{X}{W} \times \frac{1}{Y}$$

e.g. (i) 30.018 gm of tartaric acid (Mol. wt. = 150.090) is dissolved in distilled water so that the total volume of the solution is 100 c.c. (i.e. 0.1 lit), the molarity of the solution is 2M.

(ii) 16.049 gm of Ammonium chloride (Mol. wt. = 53.49) is dissolved in distilled water so that the total volume of the solution is 100 c.c. (i.e. 0.1 lit), the molarity of the ammonium chloride solution is 3.00037 ≃ 3M.

(3) Specific Gravity of Solution

To find out the specific gravity of a solution at a fixed temperature specific gravity bottle is used. Specific gravity of a solution is given by the following formula.

$$\text{Specific gravity of solution} = \frac{Y - X}{Z - X}$$

where Wt. of empty specific gravity bottle = X gm.

Wt. of Sp. gr. bottle + sodium metasilicate solution = Y gm.

Wt. of sp. gr. bottle + distilled water = Z gm

2.3 OVEN

An oven manufactured by National Scientific Works, India, was used in the present work to grow crystals at a constant temperature (fig. 2.1). It consists of (i) heating element spread over the base for obtaining uniform heating (ii) temperature regulator, comprising an energy regulator unit with indicator lamps and thermocouple connected at base and (iii) a mercury thermometer having its bulb inside the oven with a bent steam leading out of the oven at the central top edge of the door.

Energy regulator unit (dial) is calibrated in terms of temperatures so that the desired temperature can be obtained and maintained constant for a long period of time. The range of temperature is from 0° to 250°C. The stabilized power is used for controlling temperature variations within ± 1°C. The working space in the oven is 2·0 inch x 1·0 inch x 2·0 inch.

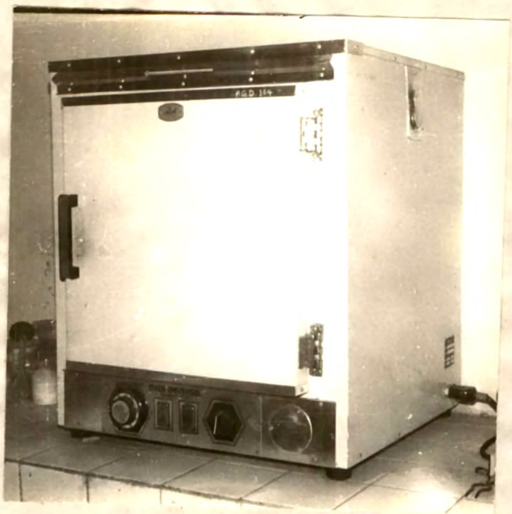

Fig. 2.1 Oven

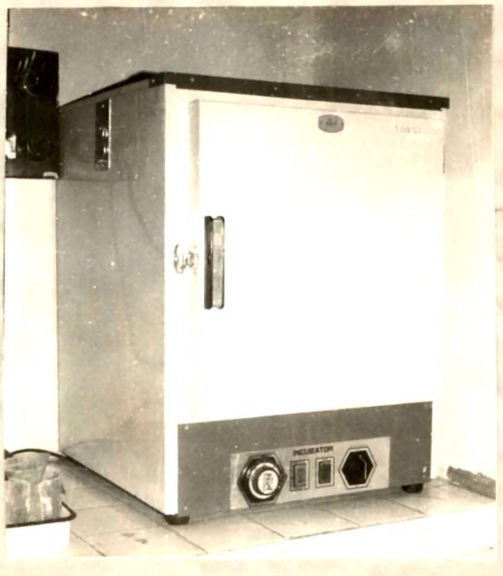

Fig. 2.2 Incubator

2.4 INCUBATOR

Since a large number of test tubes containing gel and solutions were to be kept simultaneously, incubator manufactured by National Scientific Works, India was also employed (fig. 2.2). It operates on the same principle as that of the oven described above. The range of temperatures is from 0° to 100°C. Accuracy of temperature is ± 0.5°C. Temperature can be maintained constant for long periods.

2.5 CHARACTERISATION OF CRYSTALS

Crystals grown by gel method are identified by following ways :

(i) Morphological Study

The arrangement of planes on a crystal closely follows the macroscopic symmetry implicit in its point group symmetry. Moreover, the law of constancy of interfacial angles, a fundamental law of crystallography first observed by Steno, extended by Domenico and later confirmed by Rome'de I' Isle (1972)[5] (Phillips, 1971) is universally true for crystals. The angles between the habit faces of all crystals of the same material (d-AHT) were measured to within 1° by optical goniometer and a stereogram was prepared from these observations and symmetry elements were deduced. Habit faces were also indexed in this process. The crystal class and system were then identified.

(ii) Density of Crystal

The density of the crystal was measured by specific gravity bottle.

(iii) Chemical Analysis

Microchemical analysis for the percentage contents by weight of nitrogen, carbon, hydrogen and oxygen was carried out for d-AHT crystals.[6] (Hedrickson et al., 1970). The accuracy of measurement was 10^{-6}g.

(iv) Analysis by X-ray method

The Laue method of x-ray diffraction is a powerful technique for determining the orientation of crystal. Since the crystals are transparent to x-rays, Laue transmission pattern of the crystals could be easily obtained. It was also used for the purpose of confirming the cleavage plane. The x-ray generator (Phillips No. 1009) with copper target, was operated at 35 KV and 20 mA with unfiltered beam of x-rays. Unic$\overset{a}{\text{h}}$em camera was used to take the photographs.

A~~p~~part from its extremely simple experimental arrangement, the Laue method allows ready recognition of the point group of the crystal. However, this is limited to the eleven Friedel classes (centrasymmetric groups) out of the 32 point groups. In the present case, for taking the Laue pattern, the x-ray beam was directed normal to the cleavage plane of the specimen. Besides the identification, the Laue patterns were also used for qualitative assessment of crystal perfection. Sharp and well defined Laue spots were obtained in the case of crystals free from inclusions and having low dislocation density (as measured by etchpit count). Whereas relatively distorted Laue spots were obtained with deformed crystals.

To confirm lattice parameters, x-ray Debye Scherrer powder method was employed, with CuK target. Well prepared sample was stuck on thin glass-rod and mounted in the usual way for taking photograph~~y~~ by using a ~~Weissenberg~~ Debye-Scherrer camera. The powder-photograph was analysed by Hesse-Lipson method[7] (Azaroff and Buerger, 1958) which is true only for crystals of orthorhombic system.

2.6 VERTIVAL INCIDENT LIGHT MICROSCOPE (CZ)

The vertival microscope manufactured by Carl Zeiss is one of the best and sophisticated instruments amongst the metallurgical microscopes. It can be used for different types of illuminations. Further, its utility is enhanced by providing different attachments which can be fitted to this microscope such as hardness testing unit, polarizing accessories, multiple beam interference accessories etc. For efficient use of this instrument it is imperative to be familiar with various parts, arrangements for adjustment of coarse motion brake and illuminating unit incorporating bright field and dark field, for the co-ordination of concave mirror condensers etc. Excellent account of the above is given in the instruction manual[8] supplied by the manufacturer. The basic unit of microscope consists of (i) the illuminating system (ii) the stage for placing the specimen (iii) body of the microscope carrying the objective and (iv) the monotube or binocular tube-arrangement (Fig. 2.3). The ray diagrams for bright and dark field illuminations are shown in Figures 2.4 and 2.5. The focussing arrangement is simple. It consists of fine focussing and coarse one. It is necessary to adjust the coarse motion brake.

(a) Adjustment of the coarse motion brake (Fig. 2.3)

The instrument is usually supplied with the coarse motion brake released ; hence the smoothness of the coarse motion mechanism has to be adjusted by the users. This is done by holding fast one Pinion head (1) and moving the other one in clockwise direction until the desired smoothness has been attained.

(b) Adjustment of illumination equipment

Having switched on the lamp, set switching

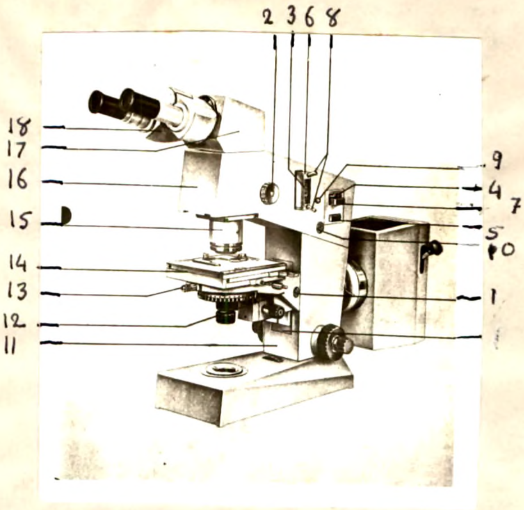

Fig. 2.3 VERTIVAL incident light microscope

1. Pinion head
2. Switching knob
3. Diaphragm
4. Diaphragm
5. Centring screws
6. Diaphragm slide
7. Filter slide
8. Centring screw
9. Centring screw
10. 12/50 lamp with adapter
11. Basic stand for incident light
12. Stage carrier
13. Tightening screw
14. Specimen stage
15. Objective on slide with concave mirror condenser
16. Carrier 'VERTIVAL'
17. Angular tube
18. Binocular straight tube

knob (2) to bright field (see para d) and on opening diaphrams (3 & 4), a bright circle becomes visible on the protective plate. This circle can be observed without eye-piece or - even better - after detaching angular tube. By turning the fixable knob so as to be loosened and moving pull-rod (not shown in Fig. 2.3) in axial direction the filament image is focussed on protective plate as critically as possible. The pull-rod is then again clamped in position and the filament image is centred by actuating centering screws (5).

(c) Co-ordination of concave mirror condensers

The co-ordination of concave mirror condensers to the objectives is to be followed according to the instructions of the manufacturer. The concave mirror and slide especially adapted for objective 25x/0.50 are marked with black point and those for objective 50x/0.80 with a white point. The following magnification values refer to the equipment of carrier VERTIVAL (factor 0.63X) with regular tube (factor 1.6X) and ~~mononuclear~~ monocular or ~~binuclear~~ binocular tube (factor 1X).

Table 2.1

Objective	Concave mirror condenser	Eye-piece			
		PK 8X	PK 10X	PK 12.5X	PK 16X
6.3X/0.12	11	50X	63X	80X	100X
12.5X/0.25	12	100X	125X	160X	200X
25X/0.50	12	200X	250X	320X	400X
50X/0.80	12	400X	500X	630X	800X
HI 100X/1.30	—	800X	1000X	1250X	1600X

(d) Bright Field : (Fig. 2.4)

For carrying out examinations in bright field the switching knob (2) has to be turned until the point to be found on it does no longer face the observer. Attention should be paid to the diaphragm slide (6) with an arrangement for luminous-field stop to bring it in centre, being inserted into the carrier to reach the maximum insertion point for proper alignment. A green filter, an attenuation filter or froasted glass may be introduced optionally or in a combined form into the filter slide (7). This slide is provided with a free

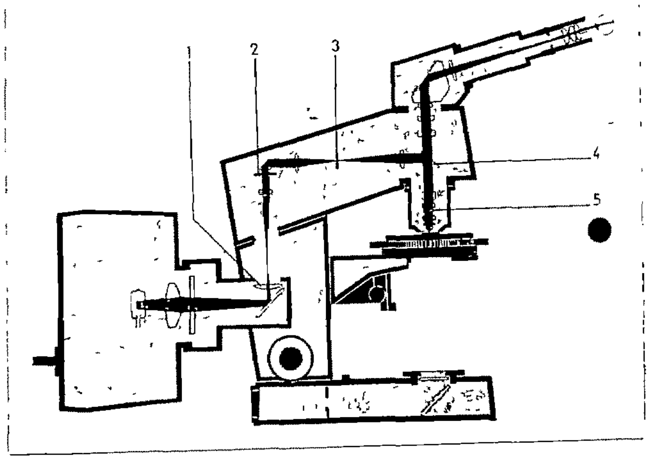

Fig. 2.4 Ray diagram for bright field

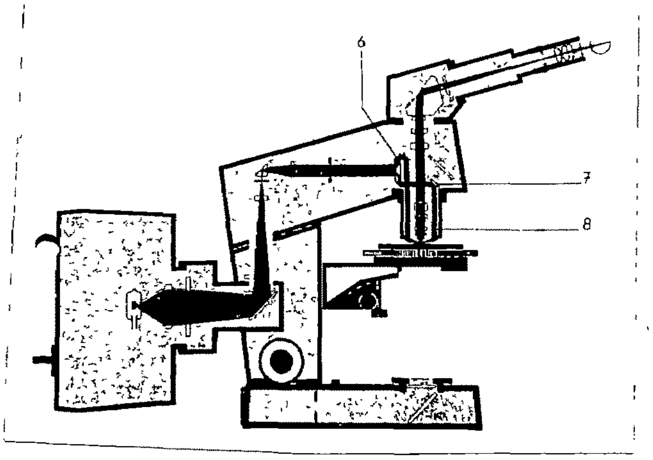

Fig. 2.5 Ray diagram for dark field

passage. Filter and shutter slides have to click indistinctly. The luminous field diaphragm is centred by actuating the two centering screws (8) and the aperture diaphragm by making use of socket wrenches to be put on to the two centering screws (9). The image of the luminous field diaphragm is to be seen within the image of the objective sharply depicted and that of closed aperture diaphragm in the exist pupil of the objective after having removed the eye-piece.

(e) Dark field : (Fig. 2.5)

For investigations in the dark field the objective corresponding to the desired magnification has to be fitted with the concave mirror condensor co-ordinated to it as mentioned above in (c). Switching knob (2) has to be set in such a way that the point to be found on it faces the observer. The luminous-field and aperture diaphragm are opened completely by actuating knurled rings (3 & 4).

(f) Camera attachment : (Fig. 2.6)

For taking photomicrographs of samples

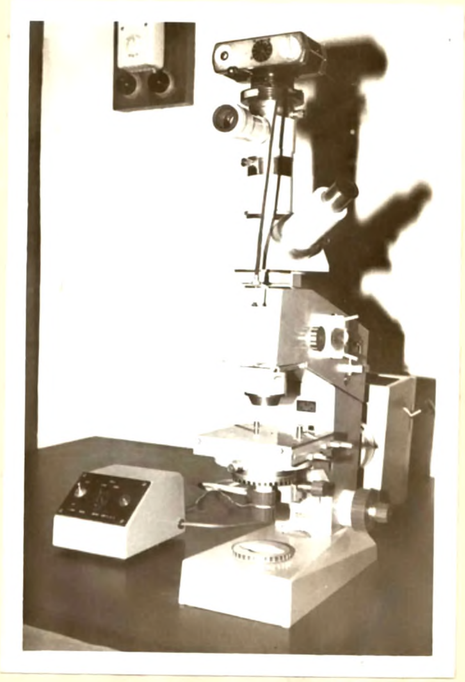

Fig. 2.6 Camera attachment on microscope

camera is attached to the microscope. The arrangement is shown in Fig. 2.6. The advantage of this method is that it is possible to observe the sample while taking photographs. Exposure times can be automatically controlled.

2.6 INDENTATION TECHNIQUE

mhp 160 microhardness tester : (Fig. 2.7)

The indenting device (19) and the threaded socket for objective (20) are mounted on a common carriage, which can be moved to and fro laterally by handle (21) in the slide (22) until it meets the stops. This makes it possible to place either the indenter device or the objective above the test specimen. The threaded socket also has a threaded collar for concave mirror condensers, so that the indentation can also be measured with peripheral dark field illumination.

A filament is attached to the upper surface of the slide for mounting the microhardness tester in the corresponding mount of an upright incident

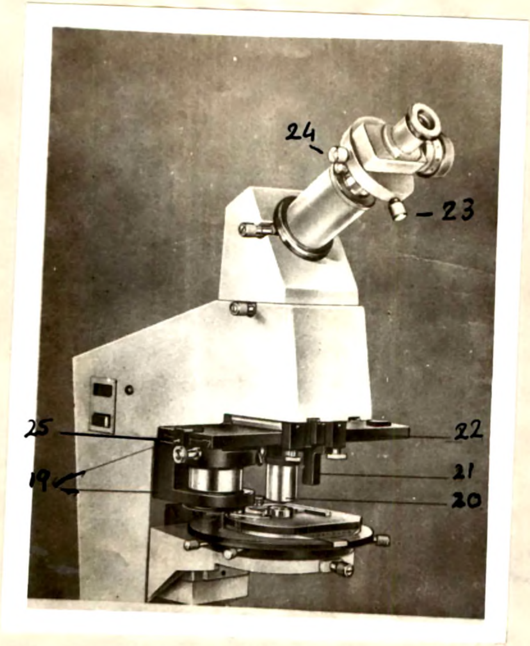

Fig. 2.7 Indentation technique

19	Indentation device
20	Objective
21	Handle
22	Slide
23	Centring screw
24	Centring screw
25	Setting screw
26	Setting screw

light microscope. The indenter device is suspended from two springs, so that it is rather sensitive to vibrations, which are manifested by continuous or intermittment swings of the index lines on the force scale. If the vibrations exceed the tolerable level or (what is rarely the case) have a frequency that is in resonance with the natural frequency of the microhardness tester, provision must be made for absorbing the vibrations of the microscope or else the latter must be set up in a part of building subject to little vibrations. Otherwise, the necessarily inaccurate application of the force, on the one hand, and the boring action of indenter on the other would result in errors that might affect the hardness readings considerably.

Various diamond indenters may be used with mhp 160 microhardness tester. Regular four-sided Vickers indenter and the Knoop pyramidal indenter with a rhombic base are employed in the present investigation. They are kept in small screw top cases when not in use. One of them can be inserted into the tester mounting by means of a special clamp. A stud on the mounting and a corresponding slot in the indenter hold provide for correct alignment. The mhp 160 microhardness tester is a sensitive instrument that requires careful handling. Dropping it will certainly result in ruining its adjustment. The microhardness tester should always be kept in closed case when not in use to avoid dust setting on it. For optimum utilization of the tester, detailed instructions for its adjustment etc. are given below :-

(1) Level the stage (14) by using highly sensitive spirit level.

(2) Focus microscope (without microhardness tester) on to an object having striking features or on to a centering cross. The object must be flawlessly prepared (naturally or artificially) and mounted on the object stage (use plane field achromatic objective and eye-piece with cross line or measuring rod).

(3) Move the object until striking features or intersection of centring cross coincides with eye-piece cross.

(4) Exchange upper tube section having eye piece for special tube with eyepiece screw micrometer and adjust.

(5) By turning the centring screws (23 & 24) bring the apex of fixed (left) measuring arm of eyepiece screw micrometer to coincide with the striking feature of object or centring cross. Both measuring arms form a cross (Zero position). (Fig. 2.8).

(6) Remove the objective with its slide.

(7) Insert microhardness tester with diamond indenter.

(8) Now screw formerly used objective into microhardness tester and place it in observation position. Critically focuss on to specimen.

(9) Centre the objective by turning setting screws (25 & 26) with socket wrench until the striking feature of the object (or centring cross) is again coinciding with apex of fixed measuring arm of dashed figure in micrometer eyepiece (Fig. 2.8).

(10) Turn the knurled knob in a counter clockwise direction (27, Fig. 2.7) to lock the indenter.

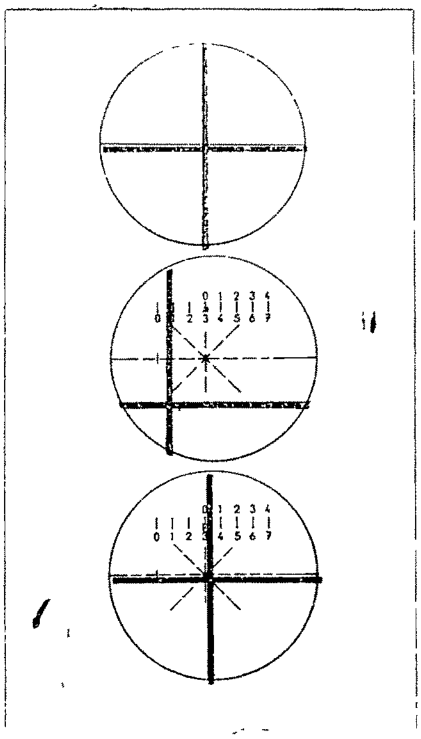

Fig. 2.8 Zero position

(11) Move the change-over slide to indenter position.

(12) Observe the horizontal bright index line of the load indicator in the eyepiece. If it is not seen, turn the rear knurled knob (28, Fig. 2.9) on microhardness tester until it is seen.

(13) Focus the line, if necessary, by adjusting micrometer eyepiece.

(14) Turn knurled knob until the index line coincides with horizontal line in the eyepiece. Should the eyepiece be oblique to the line, turn eyepiece. This fixes the initial position of index line.

(15) Apply suitable load.

(16) Observe the (upward or downward) motion of the index line within the image field.

(17) Observe with naked eye the tip of the indenter and simultaneously turn the fine motion knob of the microscope so that image of the tip is seen on the specimen.

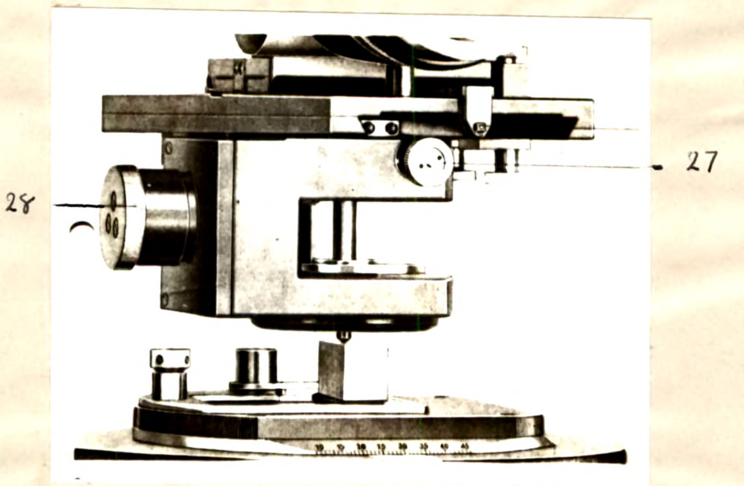

Fig. 2.9 Indentation technique

27. Knurled knob

28. Rear knurled knob

(18) Now observe through eyepiece and turn fine motion knob so that the indenter just touches the specimen.

(19) When indenter touches the specimen the index line starts moving back. Turn the fine motion knob uniformly until the index line coincides with original reference line.

(20) Turn fine motion knob in the reverse direction until the index line goes back to the same position (upward or downward).

(21) Now lower the stage considerably.

(22) Release the indenter by actuating knurled knob (27) in clockwise direction.

(23) Remove load.

(24) Move the indenter device to its operating position and lock it.

(25) Turn knurled knob, if necessary, so that bright index line coincides with the horizontal line in the eyepiece.

(26) Observe the indentation mark through eyepiece and measure the length of the indentation mark with micrometer eyepiece.

(27) Compute the hardness number by using necessary formula.

2.8 ETCH METHOD

This method[4] (Cabrera and Vermilyen, 1958) consists of carefully preparing crystal surfaces and solutions of desired composition and concentration and of dipping the prepared crystal surface in the still solution for definite time at a constant temperature of etching and then gently washing it in a solvent (alcohol) in which the crystal surface is not soluble. It is known that rinsing may deform the crystal if there is an appreciable change of temperature occurred at the time of rinsing. Hence adequate care in the present work was taken during rinsing of the crystal.

Gel-grown crystals of d-AHT were cleaved in the usual way i.e. by keeping a sharp razor along cleavage direction and then giving a sharp blow. Every time freshly cleaved crystal surfaces were used for etching work in still etchant.

2.9 LAURENT'S HALF-SHADE POLARIMETER

Optical activity of d-AHT solution was determined by the polarimeter. It consists of two nicol prisms N_1 (polarizer) and N_2 (analyser) capable of rotation about a common axis. A glass tube T, containing the optically active substance and dosed at the ends by cover slips and metal covers, is mounted between the two nicols as shown in Fig. 2.10.

Light from a monochromatic source$ S is rendered parallel by a convex Lens L and made to fall upon the polarizing nicol N_1. After passing through N_1 the light becomes plane polarised with its vibrations in the principal plane of the nicol. This plane polarised light passes through a half shade device H (called Laurent's plate) and then through the tube T containing the active substance. The emergent light, on passing through the analysing nicol N_2, is viewed through a Galelian telescope G to which is attached a scale for measuring the rotation of the plane of polarisation.

Working of the half shade device :

Half shade device (Laurent's plate)[9] (Singh and

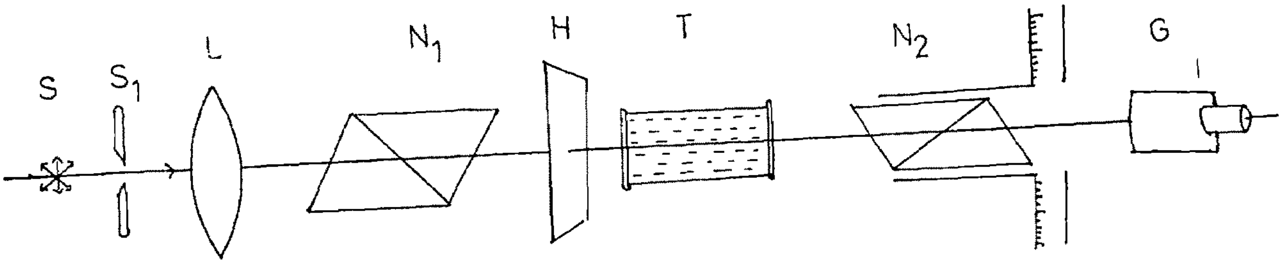

Fig. 2.10 Laurent's half-shade polarimeter

S - monochromatic source
S_1 - Slit
L - Lens
N_1 - Nicol prism as polarizer
H - Half shade device (Laurent's plate)
T - Glass tube
N_2 - Nicol prism as analyser
G - Galelian telescope

Agrawal, 1972) consists of a semi-circular plate of quartz, cut with faces parallel to the optic axis, cemented together with another semi-circular plate of glass so as to form a composite circular plate. The thickness of the quartz plate is such that it introduces a path difference of $\overset{\lambda/2}{N_2}$ (or a phase difference of π) between the O- and E- rays in transmission normally through it. Thus it is simply a half wave plate. The thickness of the glass plate is so adjusted that it transmits and absorbs the same amount of light as the quartz plate does.

The half-shade serves the purpose of dividing the field of view into two halves. The device is so accurate that if the analysing nicol is rotated through even a small angle from the position of equal brightness, a marked change in the intensity of the two halves is observed. Our eye can detect the difference in brightness of the two halves of the field very accurately when they are simultaneously presented to the eye. It, however, suffers from a disadvantage that it can be used for one particular wavelength for which the quartz half serves as a half wave plate.

Determination of specific rotation of sugar

In order to find the specific rotation of an optically active substance, the analyser N_2 is first adjusted to obtain the condition of equal brightness of the two halves of the field of view, first with water in the tube T and then optically active solution of known concentration filled in the tube. Reading of the analyser is noted both times with the help of the verniers on the circular scale. The difference in the two readings of the analyser gives the angle of rotation θ produced by the solution. The direction of rotation of the analyser gives the sense of rotation of the plane of polarization by the active substance.

In actual practice, the angle of rotation is determined for a no. of solutions of different concentrations. Then a graph is plotted between concentration C and the angle of rotation θ which comes out to be straight line. The slope of the straight line gives θ/c and the specific rotation of the solution is calculated from the relation

$$S = 10 \, \theta/lc$$

where l is the length of the tube in cm., θ is the rotation in degrees and C is the concentration of the solution in gm/c.c.

When optical rotation of liquid is clockwise the substance is dextra rotatory and when it is anti clockwise, it is Levo rotatory.

This technique was used to determine specific rotation and polarity of aqueous solution of ammonium hydrogen-d-tartrate crystals.

2.10 GONIOMETER

The interfacial angles of crystals are measured by means of instruments which are called goniometers.[5] (Phillips, 1971). There are two types of goniometers.

(i) Contact goniometer

(ii) Optical goniometer

(i) Contact goniometer

The contact goniometer consists of a protractor (least count $\frac{1}{2}^{\circ}$) which has a thin flat bar fastened at its centre rotatable along the protractor scale (fig. 2.11). The edge of the bar

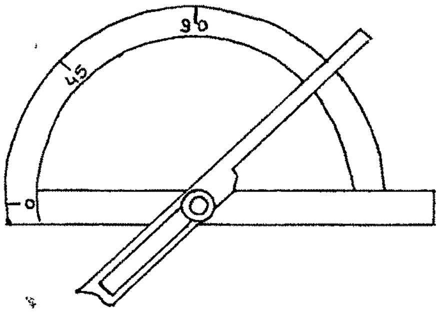

Fig. 2.11 Contact Goniometer

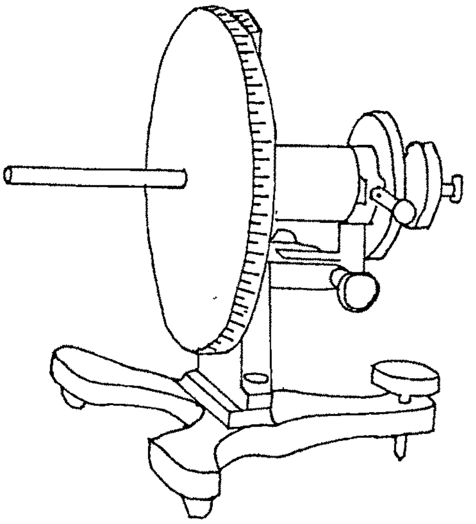

Fig. 2.12 Reflecting goniometer

or a line marked along it passing through the centre of rotation, reads the angle of rotation. The outer straight edge of the protactor and adjoining edge of the flat bar, are placed in contact with the two faces of the crystal, the angle between which is to be measured. This angle is the dihedral angle between the two faces, its suppliment is the interfacial angle.

The contact-goniometer is useful in the case of large crystals and those whose faces are not well polished, the measurements with it, however, are seldom accurate within a quarter of a degree. In the finest specimens of crystals, where the faces are smooth and lustrous, results far more accurate may be obtained by means of a different instrument called the reflecting (optical) goniometer. Estimation of interfacial angles of d-AHT crystals were made by the contact goniometer and accurate determinations were made by optical goniometer.

(ii) Optical goniometer

Optical goniometers are used to study small crystals. They are also known as reflecting goniometers. The interfacial angle between two faces of a crystal is measured by reflection of a small pencil of light, first from one face and then from the other. Usually a tiny crystal of about few milimeters can give good results.

In present case, a goniometer is used having a circular plate marked 360° degree on it with a vernier scale (Least count 30 seconds). At the centre of the goniometer is attached a rod on which the crystal to be studied is mounted. Full instrument is kept under the simple table microscope with a side bulb to illuminate the object (Fig. 2.12).

A beam of light is allowed to fall on crystal face and a reflected image is observed in a microscope by reflection first from the face 1. The crystal is then rotated about the axis of rotation parallel to the common edge of the faces, till the image of crystal surface is seen reflected from second face. The angle of rotation recorded on the goniometer is the interfacial angle. This procedure is repeated for all faces belonging to a zone. Thus all interfacial angles in a zone are measured. To measure angles in another zone the crystal is unmounted and remounted with the corresponding zone-axis parallel to the axis of rotation of the goniometer.

In present case, d-AHT exhibits only one prominent zone. To measure interfacial angles between faces other than zone faces, the goniometer is set in ~~a~~ such a way that common edge is parallel to rotation axis of goniometer. The stereographic projection is then used to determine Miller indices of all faces.

2.10 STEREOGRAPHIC PROJECTION

Stereographic projection is one of the methods of converting salient features of a three dimensioned crystal into two dimensional one. It is as follows :[5]

The plane of projection is the equatorial plane of the sphere. The vertical line through the centre of this plane touches the northern hemisphere or upper hemisphere at N and the lower or southern hemisphere at S. These points, N and S, are known as poles of the north and south hemispheres respectively. The points representing faces in the northern or upper hemisphere on the spherical projection are joined to the south pole. These lines intersect the plane of the new projection at points which represent the faces.

These points are also called poles. To represent faces of the southern or lower hemisphere, poles on the lower half of the spherical projection are projected to the central plane by lines connecting them to the north pole of the sphere. These are also the points or poles on the central equatorial plane. This plane which now represents faces of a crystal is referred to as a stereogram and the method of projection is called stereographic projection. It is conventional that on stereographic projection, northern hemisphere faces are often indicated by crosses and those in the southern hemisphere by open circles.

The characteristics of a stereographic projection are as under :

(1) All circular arcs or circles on the spherical projection are projected as arcs of true circles on the stereographic projection.

Just as each arc on the sphere measures an interfacial angle, the circular arc, on the stereographic projection determines the interfacial angle. Equal angles which are equal arcs on the spherical projection are projected as arcs or straight lines of equivalent measures or length.

(2) Those that pass through both the north and south poles of the spheremeridional lines are projected as straight lines which are readily arcs of circles of infinite radii.

(3) Poles of horizontal faces will be projected at the centre of the projection.

(4) The poles of vertical faces will fall on the circumference.

(5) Poles of faces in zone will all fall on the same arc.

(6) Symmetry planes will be represented by arcs of circles.

(7) Positions of symmetry axes are represented by points which are projections of the points of emergence of the axes on the spherical projection.

(8) The plane of projection, viz. the plane of equatorial horizontal zone circle as the

primitive circle or simply the primitive. The section of a plane passing through the centre of a sphere is always a great circle.

(9) Vertical zone-circles are projected as diameters of the primitive circle drawn in different directions. These are described as straight zones.

(10) Oblique~~s~~ zone circles are projected as axis of circles of different radii meeting the primitive each at the ends of a diameter.

It is clear from above that this projection accurately represents angular relationship between different faces on a crystal. Hence it is called angle-true projection. The representation of a crystal in this manner is a stereogram. It consists of a primitive circle, diameters drawn north-south, east-west, NE - SW and so on and arcs of circles drawn to represent oblique zones. An assembly of points representing the faces lie on these various zone circles. The points are usually referred to as faces, and the arcs and ~~dimentional~~ diametral lines as zones. Thus a stereogram of a crystal depicts (1) distribution of faces in zones (2) a a symmetry in the distribution of the faces, and (3) the interfacial angles projected on the stereogram in the form of straight lines and arcs.

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CHAPTER - 3

ERROR ANALYSIS

PAGE

* * *

3.1 INTRODUCTION

No physical measurement is absolutely correct. It is always associated with an error. The final result in an experiment is obtained after a computation involving different physical quantities which are measured in the course of the experiment. It depends on the refinements of the experimental techniques and on the method of treatment given to the different observations.[1,2] (Brinkworth, 1968 ; Baird, 1962). Relationships between different physical quantities in an experiment should be made as simple as possible, preferably linear and should be amenable to graphical analysis.[3,4,5] (Cook and Rabinowiez, 1963 ; Topping, 1955 ; Knight, 1966).

In the present work relations between hardness on cleavages of synthetic single crystals of d-AHT, expressed by a hardness number and applied load or applied load and diagonal of indentation mark on a cleavage surface or a suitable combination of different physical quantities for obtaining a straight line are graphically studied. Data are plotted on a graph with carefully chosen scales along the axes so that details are not bunched together over a small range and are commensurate with accuracy and precision of observations of the variables along the axes so as to minimize the unwanted magnification of errors associated with each observation. In the present analysis of observations, linear relationships between different physical quantities exist or arc created by having suitable combinations of these quantities. Obviously the plot between variables having linear relation is straight line. It is necessary to obtain the estimation of the best straight line. For this several methods are known. They are as under :

(i) Estimation of the best straight line by eye.

(ii) Estimation of $y = mx + c$ by the method of zero sum.

(iii) Centroid method to estimate $y = mx + c$.

(iv) Estimation of $y = mx + c$ from data used in a specific manner.

(v) Statistical estimation of best straight line.

Out of these methods, (ii), ~~(iii)~~ and (v) were utilized in the present work to analyse the data on hardness of d-AHT crystals. The straight line plots were obtained for the graphs of log d vs. log p, and log $\overline{HT}_Q$ vs. log T_Q, are presented in the concerned chapters of Part - III on hardness of synthetic single crystals of d-AHT. The details of the procedure followed in each method are briefly described here.

3.2 ZERO-SUM METHOD

This procedure is usually known as Meyer's method or Campbell's method. In an experiment independent variable x is arranged at some set value and dependent variable y is measured. Values of x are arranged in ascending order. The equations are written in the form $y_1 = mx_1 + c$ for a pair of n observations. If n is even, the first (n/2) equations are added to give

$$Y_1 = mX_1 + \frac{nc}{2} \qquad \ldots.. \quad (3.1)$$

and the second group of (n/2) equations to obtain

$$Y_2 = mX_2 + \frac{nc}{2} \qquad \ldots.. \quad (3.2)$$

solving the above simultaneous equations,

$$m = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$c = \frac{(Y_1 + Y_2) - m(X_1 + X_2)}{n} \quad \ldots. (3.3)$$

$$c = \frac{(Y_1 + Y_2)(X_1 - X_2) - (Y_1 - Y_2)(X_1 + X_2)}{n(X_1 - X_2)} \quad \ldots (3.4)$$

If n is odd, the middle equation is included in each group and the above procedure is followed for calculating m and c.

The above procedure is replaced by arranging y in ascending order and treating x as dependent variable. When the calculations are made as shown above, the values of m and c are different from those obtained above.

3.3 STATISTICAL ESTIMATION

These are two ways of estimating statistically the best straight line, (a) Regression of x on y and (b) Regression of x on y. In both these methods one variable ia assumed to be free from error :

(a) Regression of y on x :

The best straight line is one for which the squares of the deviation of every point measured parallel to y-axis and summed for all points is a minimum. This is known as regression of y on x.

Suppose there are n-pairs of observations (x_1, y_1), (x_2, y_2) .... (x_n, y_n). For each known x, it is required to predict the best value of **y** using all observations.

Let $$Y_1 = mx + C \qquad \text{..... (3.59)}$$

where Y_1 is not the observed value y, corresponding to x_1, but it is the best value considering all the observations. The difference between the actual and predicted values of **y** is

$$y_1 - Y_1 \quad \text{for} \quad y = y_1 \qquad \text{..... (3.26)}$$

Assuming an equation of the form

$$y = mx + C$$

for which values of m and C are required such that

$$\Sigma(y - Y)^2 = E \qquad \text{..... (3.71)}$$

is a minimum

$$y - Y = y - (mx + C)$$

$$E = \sum_1^n \left[y - (mx + C)\right]^2$$

$$= \sum_1^n \left\{y^2 - 2y(mx + C) + m^2x^2 + 2mxc + c^2\right\} \qquad \text{..... (3.82)}$$

differentiation of E w.r.t. m yields

$$\frac{dE}{dm} = \sum_{1}^{n} (-2yx + 2mx^2 + 2xc)$$

$$= \sum_{1}^{n} 2(mx^2 + xc - xy)$$

For minimum E, $\frac{dE}{dm} = 0$

$$\therefore \sum_{1}^{n} xy = m\sum_{1}^{n} x^2 + c\sum_{1}^{n} x$$

..... 3·9 (3.~~23~~)

sameway differentiation of E w.r.t. C gives

$$\frac{dE}{dc} = \sum_{1}^{n} (-2y + 2mx + 2c)$$

$$= \sum_{1}^{n} 2(mx + c - y)$$

for minimum E,

$$\frac{dE}{dc} = 0$$

$$\sum_{1}^{n} y = \sum_{1}^{n} c + m\sum_{1}^{n} x$$

$$= nc + m\sum_{1}^{n} x$$

..... 3·10 (~~3.24~~)

The equations 3.~~23~~9 and 3.~~24~~10, when solved for C, give

$$c = \frac{\sum y - m\sum x}{n} = \frac{\sum y}{n} - \frac{m\sum x}{n}$$

$$c = \bar{y} - m\bar{x}$$

..... 3·11 (~~3.25~~)

where $\bar{x} = \frac{\sum x}{n}$ and $\bar{y} = \frac{\sum y}{n}$

$(\bar{x}, \bar{y})$ represent the mean of all co-ordinates x and y. The best straight line passes through the mean of all co-ordinates. Substituting value of C from ($\overset{3\cdot 11}{\cancel{3.25}}$) in ($\overset{3\cdot 9}{\cancel{3.23}}$) gives

$$\begin{aligned}
\sum xy &= m\sum x^2 + (\bar{y} - m\bar{x})\sum x \\
&= m\sum x^2 + \bar{y}\sum x - m\bar{x}\sum x \\
&= m\sum x^2 + \frac{\sum y}{n}\sum x - m\,\frac{\sum x}{n}\sum x \\
&= m\sum x^2 + \frac{\sum y \sum x}{n} - \frac{m}{n}\left(\sum x\right)^2 \qquad \ldots(\overset{3\cdot 12}{\cancel{3.26}})
\end{aligned}$$

$$\sum xy - \frac{\sum x \sum y}{n} = m\left\{\sum x^2 - \frac{(\sum x)^2}{n}\right\}$$

$$\begin{aligned}
m &= \frac{\sum xy - \frac{\sum x \sum y}{\cancel{x}\, n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \\
&= \frac{\sum (x - \bar{x})\,(y - \bar{y})}{\sum (x - \bar{x})^2} \qquad \ldots(\overset{3\cdot 13}{\cancel{3.27}})
\end{aligned}$$

It is well-know that two conditions determine a straight line. Having obtained the values of slope (m) and intercept (c) the best straight line for x pairs of observations is

$$y = mx + C \qquad \ldots\ldots$$

3·14 (~~3.28~~)

where m is called the regression coefficient.

(b) Regression of x on y :

The best straight line is the one for which the squares of the deviation of every point measured parallel to the x-axis and summed for all points is a minimum. This is known as regression of x on y . It is thus clear from the above definition of the best line that equations similar to the ones derived above in (a) can be obtained by interchanging x and y and X and Y . Thus the mean co-ordinates are

$$\bar{x} = \frac{\sum x}{n} \qquad \ldots\ldots$$

3·15 (~~3.29~~)

$$\bar{y} = \frac{\sum y}{n} \qquad \ldots\ldots$$

3·16 (~~3.30~~)

and the intercept (c) and slope (m) are

$$c = \bar{x} - m\bar{y} \qquad \ldots\ldots \overset{3\cdot 17}{(\cancel{3.31})}$$

$$\text{and} \quad m = \frac{\sum (x - \bar{x})\,(y - \bar{y})}{\sum (y - \bar{y})^2} \ldots\ldots \overset{3\cdot 18}{(\cancel{3.32})}$$

and the best straight line is

$$x = my + C \qquad \ldots\ldots \overset{3\cdot 19}{(\cancel{3.33})}$$

where c and m are given by $\overset{3\cdot 17}{(\cancel{3.31})}$ and $\overset{3\cdot 18}{(\cancel{3.32})}$.

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CHAPTER - 4

GROWTH AND DISSOLUTION OF CRYSTALS

* * *

4.1 GEL - A MEDIUM FOR CRYSTAL GROWTH

4.1.1 Introduction

Existence of large and apparently perfect crystals of many minerals in nature has attracted attention of many scientists in thefield of crystallography and inspired them to grow such crystals in the laboratory. Materials required in modern devices should not only be of high purity but should also have high degree of perfection in crystalline structure with minimum defects. Such criteria can be fulfilled only by single crystals grown under the most favourable conditions. Consequently, enormous amount of labour and care has been lavished on the development of growth techniques. Several precise techniques, depending on the properties of the material to be grown in crystalline form have been invented till date.

The growth of single crystals in gels has received considerable importance since Leisegang (1896)[1] first observed the periodic precipitation of slightly soluble salts in gelation. These " Liesegang's rings " inspired many other chemists and also minerologists to study other reactions in various colloids. Among early workers were Hatschek (1911)[2], Holmes (1917)[3,4] , Fells and Firth (1926)[5], Fisher and Simons (1926)[6,7], Morse and Donnay (1931)[8] etc. Interest was revived for the method by Stong (1962)[9] and soon after him Vand et al. (1963)[10] published a note describing the full potential of growing single crystals in gels. Later a comprehensive survey of the technique by Henisch et al. (1965)[11] gave momentum to crystal growers all over the world. Since the present work deals with growth of single crystals of ammonium-hydrogen d-tartrate by gel technique, It would be appropriate to concentrate on various aspects of crystal growth in gel media.

4.1.2 Gels : Nature, Preparation and Properties

A highly viscous two component system of semi-solid nature, rich in liquid and having fine pores in it, may be referred to as 'gel'. Silica gel (synonymically) called silica hydrogel, water glass or silicate glass, usually prepared from sodium meta silicate solution) agar gel (a carbohydrate polymer derived from sea weeds), gelatin gel (which resembles protein structure), day gel, soap fluid, polyacrylamide, dense solution metal hydroxides, polyvinyl alcohol, oleates, stearates, aluminates etc., are some substances to be categorised as gels. And a sol subjected to a number of treatments such as warming, cooling, chemical reaction, addition of external reagents, can be developed for gelation[12-16] (Lyoyd, 1926 ; Hedges, 1931 ; Bartell, 1936 ; Plank and Drake, 1947 ; Alexander and Johnson, 1949).

It may be mentioned that silica hydrogel has been most commonly used, due to its far better stability than all organic gels[17,18] (Barta et al., 1971 ; Ohta et al., 1979). Though in certain specific cases gelatin gel[19,20] (Blanks et al., 1973 ; Patel and Rao, 1979), agar gel[21] (Leckebusch, 1974) and polyacrylamide[22,23] (Brezina and Hanurankuva, 1976 and Blank and Brenner, 1971), have been preferred, while in some other cases[24] (Van Rosmalen, 1976) both inorganic and organic gels have been found equally good for crystal growth in laboratory.

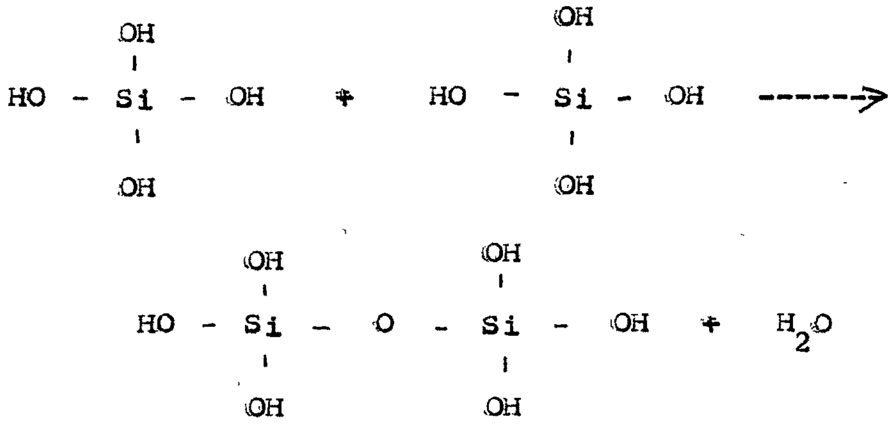
In order to obtain gel medium of desired pH, requisite amount of a suitable acid is normally added to the constantly agitated aqueous solution of $Na_2SiO_3.9H_2O$. The acidity of the resulting solution determines the course and rate of polymerization[25] (An Pang, 1963). The time of gelation varies widely from a few minutes to several days depending on the nature of materials used, their history, temperature and source. Also the mechanical properties of a fully set gel are at variance with gelling conditions.

4.1.3(i) Gelling Mechanism and Structure of Silica Hydrogels

When the solution of sodium meta silicate is mixed with any mineral or organic acid, the monosilicic acid is formed in reaction :

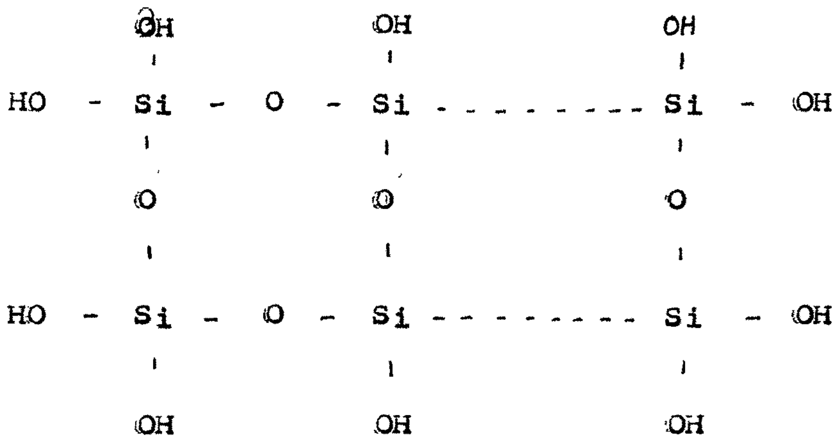
$$Na_2SiO_3 + H_2O \dashrightarrow H_4SiO_4 + 2NaOH \qquad \ldots (1.1)$$

This acid produces a dimer :



$$HO-\overset{OH}{\underset{OH}{Si}}-OH + HO-\overset{OH}{\underset{OH}{Si}}-OH \dashrightarrow HO-\overset{OH}{\underset{OH}{Si}}-O-\overset{OH}{\underset{OH}{Si}}-OH + H_2O \qquad (1.2)$$

and then a trimer and then a polymer until a three dimensional network of Si-O (siloxane) link is established.



$$\begin{array}{ccccccccccc} & & OH & & & & OH & & OH & & \\ & & | & & & & | & & | & & \\ HO & - & Si & - & O & - & Si & \text{---------} & Si & - & OH \\ & & | & & & & | & & | & & \\ & & O & & & & O & & O & & \\ & & | & & & & | & & | & & \\ HO & - & Si & - & O & - & Si & \text{---------} & Si & - & OH \\ & & | & & & & | & & | & & \\ & & OH & & & & OH & & OH & & \end{array} \qquad (1.3)$$

As the polymerization continues, water accumulates on top of gel surface, a phenomenon known as syneresis. The details about the process is given in next section. The acid added to sodium-meta-silicate serves to neutralise the NaOH of the relation (1.1). A weak acid such as acetic acid (CH_3COOH) is generally preferred unless otherwise unsuitable as gelling agent, first because the pH of the gel set with it changes only slightly with time[26] (Hard and Griffith, 1935), and secondly the mineral acids tend, more or less, to spoil the growing crystal. It is noteworthy that in less acidic gel solutions the reaction between the acid and sodium metasilicate, occurs with liberation of hydroxyl ions and thus pH of the solution rapidly increases during the process of polymerization. In highly acidic media, in contrast, there would be no change in pH except due to very little difference in the dissociation of acid of different complexities, as well as the requirements of reaction mechanism. Obviously then the pH must be a significant factor to decide the gel structure which in turn, would play a vital role in crystal growth. Doubtlessly, many other variables, characteristics of gels, e.g., nature and molarity of acid, strength and purity of sodium meta silicate, environmental temperature are no less influential to govern crystal growth in gels.

The structure of silica gel water system has been extensively investigated in many other ways and several comprehensive reviews are available[27,28] (Henish, 1970, Iler, 1955). One gel is distinguished from the other by nature of pores distribution. Biltz[29] (1927) concluded that hydrogels are characterized by two types of pores " Primary pores " of nearly molecular dimensions and much coarser " Secondary pores " which behave as more or less normal capillaries. The effective pore diameters are of the order of 50 - 100 A^{o} for silica gels. From the examination of gel with scanning electron microscope, Helberstadt et al.[30] (1969) showed that the gel consists of sheet like structure of varying degree of surface roughness and porosity, forming interconnected cells. The cell walls in dense gels have pores less than 0.1 to 0.5 μ while 0.1 to 0.4 μ for low density gels. pH during gelling has profound influence on gel structure. As pH increases the gel structure changes from distinctly box like net work to a loosely bound platelets. Gel structure has considerable influence on controlling nucleation density which is one of remarkable merits of gel growth. A progressive formation of cross-linkage gradually diminishes ~~all~~ cell size which in turh leads to a lowering of nucleation probability.

4.1.3(ii) Gel Syneresis

Graham (1864) first studied in detail phenomenon of syneresis. It is the spontaneous liberation of the liquid from a gel. This is not the dehydration occurring upon drying, as it takes place also in moist air and at low temperatures, but rather it is a kind of an internal dehydration (or desolvation) connected with shrinking.[31] (Jirgensons and Straumanis, 1954). Syneresis can be regarded as the reversal of swelling, and it is also observed in gels having a macromolecular network and lyogels. Many phenomena of syneresis have been studied thoroughly by S. Lipatov.

Syneresis is caused generally because a system is still not in equilibrium when a gel is formed, and equilibrium continues to be established in it. Because of this, syneresis occurs in the aging of unstable gels. It is observed that aging and syneresis are promoted by the concentration of electrolytes which discharge the structural elements and by an increase in temperature[32] (Voyutsky, 1978).

For lyogels, syneresis may consist in recrystallization. For macromolecular gels, they consist in the establishment of bonds between macromolecules, causing a further diminution in the gel volume. It may also result from the attainment of equilibrium in a gel when it cools, provided the macromolecular substance is not completely soluble in a medium. It can also be caused by chemical processes in the gel substance ; e.g. aqueous gels of cellulose xanthate undergoes syneresis as xanthate decomposes.

The crystals can also be grown in a gel-liquid pushed out by syneresis. The incorporated gel liquid reacts with feed solution gently added on free surface of gel. In course of time, single crystals are produced in feed solution on gel surface. Since the growth takes place in feed solution on gel surface, growth and dissolution phenomena take place simulataneously. Due to the domination of growth phenomena, the grown crystals are found to be of poor quality whereas the ~~same~~ crystals formed inside the gel are of superior quality.

In the literature, it is reported as the growth of crystals on gel surface[33] (Aleksandrzyk et al., 1981) ; however the detailed study of several factors affecting syneresis and hence size, shape and quality of crystals is not yet available. The author had made detailed study of several factors affecting the size, shape, number and quality of single crystals of ammonium-hydrogen-d-tartrate on gel surface and inside the gel.

4.1.4 Methods of Growing Crystals in Gel

The enormous flow of information related to crystal growth in gels has been divided in the following four basic parts, each one of them having special advantages which are detailed further :

(d) Reaction method

(b) Complex - decomplex method

(c) Chemical reduction method

(d) Solubility reduction method

4.1.4(a) Reaction method

Most of the work on crystal growth in gels has been done by reaction method. It has a special advantage of growing single crystals which are mostly insoluble (or slightly soluble) in water and which decompose before reaching their melting point. In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product[34] (Armington et al., 1967). The chemical reaction taking place can be expressed as :

$$AX + BY \dashrightarrow AY + BX \quad \ldots\ldots (1.4)$$

where A and B are cations, and X and Y are anions. The requirement to grow single crystals by this method are :

(i) the reactants employed here must be soluble in solvent (usually water) and product crystal must be relatively less soluble.

(ii) the gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed,

(iii) some solubility of product crystal is required in order to grow crystals of any size.[11] (Henisch et al., 1965).

Reaction method is very common method to grow single crystals in gel. Many workers have followed this method to grow single crystals such as phosphates of zirconium, titanium, tin[35] (Pyshkin, V.P. et al. 1983) and calcium[36] (Kibalczy, C.W. et al. 1984) ; hydrogenphosphates of potassium[37] (Joshi and Antony, 1979), calcium, lead[38] (Lefaucheux, 1981), and ammonium[39] (Glocker & Socst, 1969) ; molybdates of nickel[40] (Kurien and Ittyachan, 1980) ; calcium and strontium[41] (Kurien and Ittyachan, 1980) ; lead[42] (Pillai and Ittyachan, 1977) and barium[43] (Cho et al. 1977) ; perchlorates of potassium, rubiddium and Cesium[44] (Shripathi et al. 1980) ; oxalates of zinc, copper and manganese[45] (Khan et al. 1976) and cadmium[46,47] (Arora and Abraham, 1981 ; Volkova, G.A. et al., 1985) ; halides of metals such as chlorides of lead[48] (Bhat, 1981) and cuprous[49] (Henisch, 1972) ; bromide of lead[50] (Abdalkhatar and Ittyachan, 1980) ; iodides of lead[51] (Chand and Trigunayat, 1976), nickel, cobalt, manganese, potassium and rubidium[49] (Henisch, 1972), sulphates of barium, strontium[52] (Patel and Bhat, 1972) ; calcium[53] (Barta and Zemlicka, 1971) and triglicine and diglicine[54] (Tsedrik, et al. 1975) ; carbonates of lead[55] (Franke and Lenk, 1981) and calcium[56] (Schwartz, A. et al. 1971), and tartrates of potassium[57] (Kroon and Kanters, 1972), lead[58] (Abdul Kadhar and Ittyachen, 1977), strontium[59] (Ambady, 1968), cadmium[60] (Hopwood and Nicol, 1972), calcium[61] (Glasner, 1971), didymium[62] (Kotru and Raina, 1986) and lanthanium[63] (Kotru et al. 1986).

The normal experimental procedure is to prepare a gel by mixing a definite quantity and pH of aqueous solution (acidic in nature) with a definite quantity and specific gravity of aqueous solution of sodium metasilicate and allowing the resulting mixture of certain pH to form a gel in a test tube or a beaker. The feed solution (the other aqueous solution) is gently poured on the set gel. Alternatively the U-tube is employed for neutral gelation and than two reacting solutions are poured in two vertical limbs. For greater degree of lateral diffusion of ions to growth sites the modified apparatuses were devised[64,65] (Patel & Bhat, 1972 ; Patel & George, 1977). The arrangement has been successfully employed to grow single crystals of a mixed configuration (strontium calcium tartrate, $Sr_x Ca_{1-x} C_4H_4O_6.4H_2O$)[66] (Patel and Arora, 1977).

The present work reports successful use of this technique to grow single crystals of ammonium-hydrogen-d-tartrate. The details are given in Part-II.

4.1.4(b) Complex-decomplex method

The crystal growth by complex-decomplex method was first reported by O'conner et al. (1968). This method consists of first forming a chemical complex of the material of the eventual crystal to be grown with an aqueous solution of some suitable substance, called complexing agent, in which former is homogeneously miscible and then providing externally a suitable condition to decomplex or dissociate the complex formed. A standard procedure adopted for decomplexion is to steadily increase the dilution while the complex solution is diffusing through the gels. In case of growth of $CuCl_2$, the large solubility of CuCl in HCl solution and its marked decrease with increasing dilution immediately favours the growth by complex-decomplex method. The method has been successfully used to grow good ionic conductors of β-AgI[68] (Blank et al. 1967), α-HgS, β-HgS[69] (Shiojiri et al. 1978).

4.1.4(c) Chemical Reduction Method

This method is suitable for growing only metal crystals. Hatschek and Simon[71] (1912) grew gold crystals by adding 8% oxalic acid solution over gel which contained gold chloride solution. Single crystals of gold of triangular and hexagonal habits[72] (Kratochvil et al. 1968) of lead[73] (Liow et al. 1972), of copper[74] (McCaulcy et al. 1969) and of cupric oxide[75] (Blank and Branner, 1969) were grown by this method.

4.1.4(d) Solubility Reduction Method

This method is particularly useful for growing single crystals of highly water soluble substances.

Glocker and Soest[76] (1969) first reported the growth of dihydrogenphosphate (ADP) single crystals by this method. The substance to be grown is dissolved in water and incorporated with the gel forming solution. After the setting of gel, a solution which reduces the solubility of the substance is added over the gel to induce crystallization. Sodium chloride crystals have been grown by adding concentrated hydrochloric acid (above 5.0 N) over the gel containing a saturated solution of sodium chloride[77] (Desai and Rai, 1980). The formation of crystal is due to the reduction of solubility of sodium chloride in the liquid phase by concentrated HCl. KDP crystals were grown by reducing solubility using ethyl alcohol[78,79] (Joshi and Antony, 1978), Brezina and Havrankova, 1971).

4.1.5 Studies on Gel Grown Crystals

The gel method is capable of yielding crystals of high optical perfections of a variety of materials which have had research applications. Gel grown PbI_2 crystals have been studied to understand their band structure[80,81] (Henisch and Srinivasagopalan, 1966 Dugan and Henisch, 1967) and polytypism[82,83] (Hanoka et al. 1967; Mahesh Chand and Trigunayat, 1975).

These studies have been impeded for want of suitable specimens and many contradictory results were reported. The electrical resistivity of gel-grown lead sulphide crystals[84] (Blank et al. 1968) was found to be 8.4×10^{-4} ohmcm at $25^{o}C$, while it was 8.2×10^{-2} ohm cm for untreated natural galina and 7.0×10^{-3} ohm cm for synthetic lead sulphide[85] (Brebrick and Scanlon, 1954). A single filament of gel-grown silver acetate revealed stresses of 1.25×10^{-6} psi in bonding without fracture or permanent deformation[86] (Boulin and Eillis, 1970). Dendrites of metallic lead have been used for metallurgical studies by Bedarida (1964)[87]. Optical absorption spectra of gel-grown lead oxyiodide were studied at 430 μ . Its dielectric constant at 10 KHz is about 10.5 and magnetic susceptibility is - 0.256×10^{-6} C.G.S. units. The quality of gel-grown KDP crystals[78] (Joshi and Antony, 1978) was judged by studying dielectric properties in the vicinity of ferroelectric phase transition. Nassau et al.[88] (1973) and Abrahams et al.[89] (1973) studied structural, optical and magnetic properties of copper iodate crystals grown in gel.

4.1.6 Nucleation and Growth Mechanism

To suppress nucleation, whether it is homogeneous or heterogeneous and to stabilize the concentration gradients, in the neighbourhood of growing crystals by suppression of convection currents are the two principal functions of gel. In most of the cases homogeneous nucleation is observed. It involves the concept of critical nucleus. As a result of statistical accident, a number of atoms or ions or molecules can come together and form a rudimentary crystal. This crystal is likely to dissolve again unless it reaches a certain critical size. Beyond this size, the energy relations favour continued growth. The heterogeneous nucleation can occur in the presence of some foreign particles. Systematic experiments with the filtering media to avoid heterogeneous nucleation could not succeed fully because the nuclei are too small and most of the filters appear~~s~~ to add some particles while they subtract others. In all gel-growth systems, crystals become increasingly scarce and more perfect with increasing distance from gel interface as the slow diffusion leads to more perfect crystals.

As far as the mechanism by which crystals grow in gels is concerned there have been evidences to two-dimensional piling and spreading of growth layers, predominantly taking place[90] (Sangwal and Patel, 1974) from one or more initiation centres. One is, therefore, tempted to make comparison with solution grown crystals. When single crystals of slightly soluble salts are grown from highly supersaturated solution which just remains stable over long periods by slow evaporation or cooling, the crystals never grow larger, because the supply of solute to the crystal surfaces is still extremely feeble. The fact that the large crystals are obtainable in gels proves that the supersaturation near the surface of these crystals must be much higher in gel than in solution. This prevents the development of heterogeneous nuclei, so only homogeneous nucleation is left which is known to occur at high supersaturation only. What in fact, goes on in the medium is the diffusion of dissolved matter as a consequence of the casual character of thermal motion of molecules. The molecules pass through an energy barrier wi$\overset{d}{t}$h ΔG, the free energy of activation for the molecular transport process. A molecule or anion changes its place with a frequency.

$$\mathcal{T}^{-1} = \frac{kT}{h} \exp\left[-\frac{\Delta G}{kT}\right] \qquad \text{..... (1.5)}$$

But according to Einstein[91] (1906) the root mean square displacement λ is connected with time $\mathcal{T}$ by

$$\lambda = (2D\,\mathcal{T})^{\frac{1}{2}} \qquad \text{...... (1.6)}$$

where D is the diffusion constant.
Putting $\lambda =$ d, the ionic diameter, the frequency of nucleation is

$$F = \mathcal{T}^{-1} = \frac{2D}{d^2} = \frac{KT}{h} \exp\left(-\frac{G}{KT}\right) \qquad \text{.. (1.7)}$$

The energy Δ G is, of course, equivalent to Ec, the energy available for the creation of crystal nucleus given by

$$E_c = \frac{16}{3} \frac{\sigma^3}{\varsigma^2} \frac{\pi}{L^2} \qquad \text{.... (1.8)}$$

where σ is the surface energy per unit area, ς is the droplet density and L is the heat of desolvation. According to Fick's law :

$$\underline{\mathcal{J}} = - D \text{ grad } C \qquad \text{.... (1.9)}$$

and $$\frac{dc}{dt} = D \nabla^2 C \qquad \ldots\ldots (1.10)$$

where $\mathcal{J}$ is the quantity of matter transporting in the direction of the concentration gradient per unit area perpendicular to ∇C. Assuming that the precipitates are not too close to one another, as is true of growth in gel, the concentration in space around the crystal of radius R is a function of the distance from the centre, and the boundary conditions become

$$C(x, 0) = C_{\infty}$$

$$C(R, t) = S$$

$$C(\infty, t) = C_{\infty}$$

The solution of equations (1.6) and (1.7) gives the radius R as a function of speed V of the advancing growth fronts in gel,

$$R = \left[DV\ (C_{\infty} - S)t \right]^{\frac{1}{2}} \qquad \ldots\ldots (1.11)$$

Since each particle is to be treated independently of the others, the factor $V(C_{\infty} - S)$ is small, and hence equation (1.11) reduces to

$$R^2 = (Dt)^{\frac{1}{2}} \qquad \ldots\ldots (1.12)$$

The equation (1.12) represents one-dimensional diffusion process and has been experimentally verified by Liaw and Faust (1971).[92]

4.1.7 Advantages of Gel Technique

Of the various techniques for the growth of single crystals from melt, vapour or solution, those requiring elevated temperatures have the following inherent diffuculties.

1. Crystalline imperfections are more apt to occur due to the lattice disruption by pronounced thermal vibrations.

2. The chances of lattice contamination by impurities are profusely increased due to latter's higher solubility at higher temperatures.

3. Point defects and lattice strains are frequently introduced into the growing matrix during the range of cooling cycle.

If all the method for crystallization at room temperature, the gel method is believed to hold substantial promise of future development due to the following advantages :

(1) The crystals can be observed practically in all stages of their growth.

(2) The gel medium prevents convection currents and turbulence.

(3) By remaining chemically inert and harmless the gel framework acts like a three dimensional crucible in which the crystal nuclei are delicately held in the position of their formation, thereby preventing damage, if any, due to impact with ~~their~~ the bottom or the walls of container.

(4) The gel is soft and yields mechanically to the growing crystals.

(5) Thermodynamic considerations reveal that since the growth proceeds at or near ambient temperature, the grown crystals would contain relatively less equilibrium concentration of defects.

(6) Since the gel reduces, in effect, the speed of chemical reaction, crystals could be made to

grow much larger than those formed by a similar reaction in water or in molten state by double decomposition process.

(7) All the nuclei are spatially separated whereby the detrimental effects of precipitate-to-precipitate interaction are drastically diminished.

(8) One can control diffusion rates and nucleation probability and thus design one's own crystallization equipment for obtaining different sizes and morphology of different crystals.

(9) The growth procedure is highly economical, it yields a good crop of crystals with the simple and almost inexpensive equipment. The method can be exploited even in smaller laboratories which do not possess sophisticated equipments to grow perfect crystals.

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4.2 THEORIES OF CRYSTAL GROWTH

4.2.1 Introduction

The brief and general review of the crystal growth in a gel medium indicates the ability of a crystal to grow in predetermined geometrical shapes bounded by plane faces. Since the rates of growth of crystals are, in general, functions of the supersaturation of the fluid from which they grew, it may be asked how the surface of a crystal can grew truely plane, when in many cases the conditions of supersaturation may vary from point to point on the surface. Further why should certain faces grow at the expense of others ? What is the mechanism of formation and development of like and unlike faces during crystal growth ? There are many questions on various aspects of crystal growth which are not yet fully answered. The section reviews in brief different theories of crystal growth.

Crystallization can be regarded as a two stage process, nucleation and growth. A complete understanding of crystal growth requires the knowledge of many a discipline such as equilibrium thermodynamics, irreversible thermodynamics, chemistry, surface science, heat transfer, mass transfer, crystallography, etc. There is a voluminous literature on the various existing theories of crystal growth. These have been extensively covered by Buckley (1958)[1], Verma and Krishna (1968)[2], Strickland - Constable (1968)[3] and others. Without going into their mathematical intricacy they can be summed as follows :

Essentially, the theories can be divided into two parts : the growth of ideally perfect crystal and that of an imperfect one. An ideal crystal is one in which each atom is symmetrically surrounded by neighbouring atoms in a regular geometrical configuration. As against this, an imperfect crystal is one in which the relative positions of the atoms differ from those of an ideal lattice by amount comparable to an interatomic spacing.

4.2.2 Growth of a Perfect Crystal

In the first quantitative theory of crystal growth, given by Gibbs in 1878, based on thermodynamic grounds, an analogy is made between the growth of a water droplet in a mist and the growth of a crystal. It is agreed that only those crystals develop which would lead to a minimum surface free energy for a given volume. In 1885 Curie calculated the shape and end forms of the crystal in equilibrium with solution or vapour consistent with the conditions of possessing a minimum sum total of surface free energies. In 1901 Wulff further extended Curie's theory by measuring growth velocities of different faces, Marc and Ritzel (1911)[4] modified Curie's theory by considering the influence of surface tension and solution pressure, i.e. solubility. When the differences in the solubilities are small, growth is influenced by surface energy and any increase in the surface of one form is necessarily at the expense of the other. It was suggested by Lecoq de Boisbaudran in 1879 that different forms might exhibit difference in solubility.

Berthoud (1912)[5] and Valeton (1951)[6] assailed Curie's theory on the ground that greater supersaturation would cause rapid growth and consequently, the crystal habit ought to approximate to the spherical shape, a contradiction to the commonly observed fact. The more rapid the growth the simpler the crystal becomes until one single form predominates with the practical exclusion of all others.

Between 1920 and 1940 Kossel (1927)[7] Stranski (1928)[8], Volmer (1939)[9] and others built up a conventional theory on the mechanism of crystal growth. The theories suggest that growth occurs by spreading of layers of constant thickness across the face and the thickness of the layers must be very small as compared to the distance between the advancing fronts. The repeatable step theory is based on a particular molecular mechanism for the attachment of molecules whereas the layer by layer theory is of a general nature since nothing is assumed here.

Experiments indicate that in the growth from solution or vapour, the rate of direct arrival of molecules at any particular point on the crystal surface is generally small compared to the rate of indirect arrival through surface migration. Volmer (1939)[9] suggested that adsorbed molecules would be able to migrate freely over the surface and might change sites a large number of times before evaporating. Layer mechanism of growth has been extensively studied by Bunn and Emmet (1949)[10], Griffin (1950)[11], Forty (1951)[12], Williams (1957)[13] Buckley (1958)[1] and Sunagawa (1962)[15].

4.2.3 Discrepancy in Growth Theory

The theory of growth at the kink sites, even though assisted by surface migration, becomes less satisfactory to account for the observed rate of spreading of layers and still, to explain the rate of surface nucleation. Calculations for the concentration of kink in steps and the rate of diffusion of molecules led (Burton et al. (1931))[16] to the conclusion that at normal supersaturation the rate of surface nucleation would be immensely small, and to obtain an observable growth rate, a large supersaturation of at least 25-50% is required. Above this value of supersaturation, the growth is not limited by nucleation and an ideal crystal will be able to grow layer-by-layer. Real crystals do, however, grow at observable rates at supersaturation of 1% or lower[17] (Volmer and Schultze 1931) ; indeed the crystals grown at such low supersaturations are almost well faceted and of high quality with respect to normal defects. The theoretical prediction of the rate with which a crystal should grow at this saturation turned out to be too small by a factor 10^{1200}. Since there is a record discrepancy between theoretical and experimental growth rates nucleation theory was rechecked, but found to be correct.

4.2.4 Growth of Real (Imperfect) Crystals

In an attempt to explain the disparity between theory and experiment, Frank (1949)[18] drew attention to the probable role of screw dislocation in furthering the growth process. The emergence of screw dislocation on a crystal face produces a ledge of height equal to the Burgers vector. If the crystal is pictured as growing by the attachment of molecules to the edge of this ledge, then no surface nucleation is necessary since the ledge is self-perpetuating and continues to be present on the surface, so long as the dislocation line intersects the surface. As the growth proceeds on the surface, the edge winds itself into a spiral centered on the dislocation itself. Since the turns of the spiral will be closed together, a large portion of the molecules adsorbed will reach the ledge before re-evaporation. Direct evidence for the occurrence of spirals on grown faces was obtained by Griffin (1950)[11] on beryl and subsequently by Verma (1951)[19], Amelinckx (1951)[20], Forty (1954)[21] and others on a variety of crystal surfaces.

4.2.5 Criticism of Screw Dislocation Theory

Though the experimental observations in support of the theory of spiral growth increased considerably, there were contrary ideas about several aspects of it. The step heights of growth spiral, e.g. in SiC are often too large to be understood in terms of screw dislocations and Buckley (1952)[22] suggested their formation to be connected with microscopic events occurring in the vapour adjacent to the surface at the moment of solidification. Jagodzinski (1954)[23,24] suggested that the high energy required for the creation of a screw dislocation could not come from the crystal structure until the crystal had grown to a considerable volume. The screw dislocations will, therefore, play a role only in the later stages of growth, thereby determining the surface structure but not the crystal structure. This was further supported by Knippenberg's observations (1963)[25] on SiC crystals.

It appears that screw dislocation theory, despite many set backs, explains several facts associated with the phenomenon of polytypism in crystals. It may be mentioned that the VLS mechanism put forth by Wagner et al. (1964)[26] and Wagner and Ellis (1964)[27,28] the atoms dissolve in a molten metal alloy phase from the vapour and condense in turn from the liquid phase into the crystal surface.

4.2.6 Whiskers, Needles and Platelets-Growth Mechanism :

Whiskers or filamentary crystals are of particular interest due to their fast growth along an axis which is often not a unique crystallographic axis. The inference is that whiskers contain axial screw dislocation which determines the fast growth direction. The side faces of whiskers are low energy planes which grow slowly or not at all. Sears (1955)[29] has found that there is a critical supersaturation above which whiskers of Cd, Ag, Zn and CdS do not grow. For whisker growth supersaturation on the side faces must be sufficiently low to prevent two dimensional nucleation which would allow radial growth. If low energy planes are parallel to a unique crystallographic axis, needles are produced. At supersaturation too high for whisker growth, platelets come into being.

4.2.7 Dendritic Growth Mechanism

The name ' dendrite ' comes from the Greek word for " tree " and denotes any tree-like branched structure (Tiller, 1964).[30] A typical dendrite consists of a primary stem onto which grow secondary branches and on these grow the tertiary branches. This frequently occurs in one plane but three-dimensional dendrites are also observed. Dendrites have been found almost invariably in metals and is common in crystals from solution, melt and vapour. Dendrites are normally single crystals and the branches follow definite crystallographic directions. The opposite sides of the dendrite exhibit remarkable symmetry and branches are often spaced out at regular interval. Originally, a dendrite was thought to be the result of a growth protrusion of a crystal surface. It was felt that the protrusion would be in a position to collect more material and hence grow more rapidly than rest of the crystal surface (Chalmers, 1954).[31] Though a currently believed cause of such an abnormal growth is known to be the large supersaturation (rapid deposition) no definite explanation regarding the regularity of dendritic branching has been completely accepted so far. At times, dentrites whose limbs are not related to definite crystallographic directions are also observed. Details of the theories of dendtritic growth are given by Buckley (1958).[1]

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4.3 CRYSTAL DISSOLUTION

4.3.1 Introduction

Crystal dissolution and evaporation take place by the retreat of monomolecular steps across the crystal surface, a process reverse of growth. In the dissolution of a smooth face, atoms or molecules must be removed from crystal steps just as they must add to a step during growth. In crystal dissolution new steps may be initiated by two dimensional island or at a screw dislocation. In addition to these, during dissolution, steps may also be initiated at the edge of a crystal, or at edge dislocation. Therefore, dissolution is often found to be controlled by mass transfer, particularly for polycrystalline materials which have preferential sites for initiation of steps. This phenomenon is ar observed by Marangozis and Johnson (1962), Askew and Beckmann (1965) Hixon and Baum (1942) and Kassnerg (1967).[1-4]

Under a slight undersaturation, there is a tendency for pits to form at emergent dislocation sites. This tendency is often generally amplified by the presence of impurities, which are thought to adsorb on the steps and greatly retard the removal of atoms. Gilman and Johnston (1956), Ives and Baskin (1965) and Wanger (1949)[5-7] found the formation of pits in the above manner.

4.3.2 Nucleatiom of Etch Pits

The first theoretical treatment of the nucleation of etch pits at dislocations was given by Cabrera and Lavine (1956).[8] They postulated that the strain energy localized in the vicinity of a dislocation, lowered the free energy required for the nucleation of a cavity of unit depth at the site of intersection of dislocation with a crystal surface. This leads to the preferential dissolution of dislocation sites on the surface. Gilman (1960)[9] has criticized this model because elastic strain energy of a pure screw dislocation is zero at the surface and both types of dislocations (having some finite energy at the surface) seem to be etched in almost identical fashion. He has suggested that the dislocation core energy is more important than the elastic strain energy for nucleation of etch pits. This is supported by the following observations : (i) The dislocations in metals are more difficult to etch than those in ionic or covalent crystals (ii) The core energies of dislocations in metals are less than in other types of materials while the elastic strain energies of dislocations are about the same for all materials. (iii) Since overlapping strain fields of dislocations closed together tend to cancel out, it would be expepted on the basis of Cabrera's model that widely separated dislocations would etch at different rates than ones closely spaced. Contrary to this, it is observed that etch pits at isolated dislocations within the subgrains of a crystal are of the same size as the etch pits in the sub-boundaries. (iv) Dislocations were etched at different rates (Gatos and Lavine 1960)[10] Schaarwachter (1965)[11] has modified Cabrera's treatment taking due care of core energy suggested by Gilman. He distinguished three cases depending on the relative importance of the contributions of the dislocation core energy and elastic energy. (a) Only the core energy is important in lowering G (change in free energy of a two dimensional nucleus formed at dislocations). This is probably the case for metals. (b) Both the core and strain energy contribute to lowering of G ; this is possibly the case for ionic and covalent crystals with small Burger vector. (c) Only the strain energy of dislocation is significant and the Cabrera's model is valid. This case applies to materials having large Burger vectors e.g. organic materials.

4.3.3 Formation of Visible Etch Pits

The necessary condition for the formation of visible etch pits is governed by the kinetics of dissolution ledges as they move across the crystal surface during dissolution. Successive monomolecular ledges usually sweep across closed packed surface. In order for an etch pit to be visible under an optical microscope, the slope of the etch planes should be at least about 3° with respect to a close packed surface. Experimentally measured etch pit slopes for several successful dislocation etching solutions have indeed, been found to lie in the range of 5-12°. For an etch pit to have a sufficiently steep slope the ratio of dissolution velocity V_n (normal to surface) to V_l (lateral or ledge dissolution velocity parallel to surface) must be greater than a certain value, 0.1. In addition to this, the normal dissolution velocity at a dislocation (V_{nd}) be greater than the average vertical dissolution velocity (V_{ndf}) of a dislocation free portion of the surface. The necessary conditions can thus be written as

$$V_n/V_l \geqslant 0.1, \quad V_{nd} \geqslant V_{ndf}$$

Shah (1976)[12] found that for better quality of etch pits, on calcite cleavages, the ratio of tangential velocity V_t (or V_l) to V_{ndf} should be greater than 10 and the value of activation energy for tangential movement of steps away from the source, E_t, should be greater than activation energy for surface dissolution, E_s, i.e.

$$V_t / V_{ndf} \geqslant 10, \qquad E_t / E_s > 1$$

For a symmetrical pit, all planes forming a pit are equally inclined, while slopes of these planes are different for asymmetric pits. A detailed study of slopes of etch pits was systematically carried out by Ives and McAusland (1968)[13]. They have classified pits into three categories, depending upon the various ranges of slopes of pits on (0001) surface of zinc crystals. They reported that planes of the etch pits were vicinal faces.

Impurity may segregate around dislocation in impure crystals. Impurity may enhance greater chemical reactivity, giving rise to preferential two dimensional nucleation in metal crystals. It is normally observed that etch pitting solutions for most of the metals and semiconductors studied so far are strong oxidizing agents. It is presumed that the first step in the dissolution process is an oxidation of crystal surface. This is followed by the removal of oxide layers. It was observed that oxide nuclei were formed on pure copper crystals (Young, 1960)[14] and on Ge crystals (Faust, 1963).[15] However, these oxide nuclei were not related to dislocations. The influence exerted by impurities on and around dislocations has been discussed in detail by Gilman et al. (1958)[16] on LiF crystals which was etched by water with addition of impurities such as FeF_3, AlF_3 etc. They found that nature of etch pits was dependent on the concentration of FeF_3 solution. The function of FeF_3 is to inhibit the ledge motion. It means that V depends upon Fe^{+++} concentration. The Fe^{+++} ion (and such others in about 30 compounds) retards the step motion apparently by adsorption on the steps but does not seem to affect V_{nd}. Cations (Fe^{+++}, Al^{+++} etc) are believed to have strong tendency to form (FeF_6), (AlF_6) complexes and that is why, they play a major role and anions do not effect the pit formation. Cabrera (1956)[8] examined theoretically the conditions for the formation of etch pits and oxide nuclei at dislocations. He observed that the energy associated with dislocations having large Burger Vector, is sufficient to cause etch pit or oxide nuclei. Sears (1960)[17] reviewed theory of Cabrera and modified it by including the effect of solution poison. Step poison increases the rate of two dimensional nucleation at fixed supersaturations but markedly decreases the rate of step/motion or of spreading of newly formed layers. Ives and Hirth (1960)[18] studied the etch pit profile as a function of concentration of LiF and FeF_3 in the etching solution. The results were consistent with a mechanistic theory involving dissociation of LiF from unimolecular steps on it and subsequent diffusion into solution if a time dependent adsorption of FeF_3 poison at the receding unimolecular steps was involved. The above theory deals with 'part diffusion part inhibitor control of ledge kinetics'. It explains very well other results except slope of pits. According to this theory, the slope of ~~pits~~ dislocation pit should decrease with decreasing under-saturation of LiF. Experiment showed the pit slope to be essentially independent of LiF concentration. The explanation given for the discripancy was that the accumulation of an inhibitor on a given ledge increased as the distance between ledge and surface increased i.e. it was a time-dependent process. Westwood (1961)[19] used aqueous solutions of a long chain fatty acids to reveal the point of emergence of dislocations in LiF. This shows that fatty acid may provide a ready source of potential inhibitors for a variety of crystal-etchant system. Chemisorption and complex formation in this process is likely to affect the core energy available for the nucleation of kinks. Ives and Ramchandran (1967)[20] studied the morphology of etched LiF surface with an electron microscope. It reveals complex structure of surface ledges on (100) cleavage face of this crystal. The ledge structure is complex due to irregular inhibition by Ferric ions. Haribabu and Bansigir (1969)[21] after studying the role of poison and undersaturation of the etching mechanism, concluded that the stability of the complexes formed at the kink site and those formed in the solvent layer very close to the crystal surface played an important role in the formation of etch pit. Frank (1958)[22] and also Cabrera and Vermilyen (1958)[23] then applied the theory of kinematic waves to the localized dissolution process. They showed that the role of adsorbed impurity was to promote the bunching of the outward spreading dissolution terraces so that sharp edge depressions were formed which were clearly visible in microscope.

It is known that the optical resolution of a microscope is inadequate to observe the atomic steps or the small bunches of steps in the pit nucleation and early stages of growth. How do steps move during the etching of a crystal ? Where does a ' poison ' act ? How does it act for inhibiting the motion of steps ? What is the exact role of a poison ? The present theory is not yet developed to the extent of answering convincingly these questions.

4.3.4. Implications of Selective Etch

Etch pits essentially reveal the emergent points of dislocations on the surface, and therefore they give a direct measure of dislocation density[24]

(O mar et al., 1954). Since they have a definite depth, they may also give useful information about the kind, configuration and inclination of dislocations. Etching has, further been applied to study.

(i) growth history of crystals[25,26] (Pandya and Tolansky, 1954 ; Ram et al. 1973),

(ii) stress velocity of individual dislocation[27] (Gilman and Johnston, 1960),

(iii) deformation patterns like pile-ups, polygon walls[28-32] (Amelinckx et al., 1960 ; Ram and Singh, 1976 ; Desai and John, 1979 ; Pandya and Pandya, 1961 ; Saraf, 1971),

(iv) dislocation multiplication and movement[27] (Gilman and Johnston, 1960),

(v) origin of dislocations in as-grown crystals[33,34] (Wash, 1959) ; Kishan Rao and Sirdeshmukh, 1983),

(vi) fresh and grown in dislocations[35] (~~Voinova and Bereshkova~~, ~~1985~~), (Gilman et al 1958)

(vii) plastic flow around indentation[36] (Voinova and Berezhkova, 1985),

(viii) radiation hardening[37,38] (Aerts et al., 1959 ; Patel and Desai, 1969),

(ix) fracture and dislocations[39] (Stokes et al. 1959),

(x) Surface orientation determination[40] (Watenable and Sumiyoshi, 1976),

(xi) polarity of crystal lattice[28] (Amelinckx et al. 1960),

(xii) reaction mechanism[41-43] (Popkova et al., 1969 ; Bhagira 1982 ; Shah, 1984).

(xiii) grain boundaries[44] (Vogel et al. 1953).

(xiv) the formation of dislocations with different Burgers Vectors[45] (Sangwal et al. 1977),

(xv) inclination of dislocations with the observational plane[46,47] (Mehta, 1972 ; Shah, 1976),

(xvi) influence of impurity on the etching[48] (Koziejowska and Sangwal, 1986).

The present work reports chemical dissolution of gel-grown crystals of ammonium hydrogen d-tartrate with the express purpose of assessing in a qualitative manner their perfection. Attempt is also made to correlate etch patterns with the morphology of grown crystals.

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