PART-I

PART - I

GENERAL INFORMATION ON

SODIUM NITRATE AND CALCITE

EXPERIMENTAL TECHNIQUES

AND

ANALYSIS OF STRAIGHT LINE PLOTS

CHAPTER - I

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1.1 GENERAL INFORMATION ON SODIUM NITRATE

1.1.1 INTRODUCTION

The mineral sodium nitrate known as salt-peter, by virtue of its size and perfection of its crystalline structure has attracted the attention of crystallographers. Its resemblance with calcite is excellent. Several text books on minerology provide information about mineral salt-peter which is naturally available as sodium nitrate. However Dana and Ford[1] had presented excellent account of this mineral. A brief account of some of its features is given below :

1.1.2 OCCURRENCE

The natural nitrates are few in number, relatively soluble in water and with exception of soda-niter are of rare occurrence. Sodium nitrate is found as an efflorescence upon soil or in sheltered places. Usually it is associated with niter, nitro caliche, gypsum, epsomite, mirabilite and halite. The impure form of sodium nitrate is known as salt-peter (caliche). It is normally found in arid regions.

The principal deposits occur in belt roughly 450 miles long and 10 to 15 miles wide along eastern slopes of the coast range in the desert of northern Chile. Small deposits are in Bolivia, Peru, North Africa, Egypt, U.S.S.R., India and Western U.S.A. Synthetic crystals are available easily by evaporation of the water solution.

1.1.3 CRYSTAL COMPOSITION

Sodium nitrate, a nitrate of monovalent metal sodium has formula $NaNO_3$ ($Na = 27.05\%$ and $NO_3 = 72.95\%$). The natural crystal may contain Ca replacing Na atoms. Its derivation is from nitric acid and sodium carbonate and also from chile salt-peter.

1.1.4 SODIUM NITRATE GROUP AND ITS STRUCTURE

Sodium nitrate belongs to Hexagonal-R scalenohedral $-\bar{3}\,\frac{2}{m}$ with a:c :: 1:0.8726 ; $\alpha = 102^{\circ}-46.5'$ $\lambda = 73^{\circ}-30'$. In figure 1.1 small circles at the corners of unit cell are nitrogen atoms and big circles are oxygen atoms. The cleavage is outlined by thick lines. Fig. 1.1 gives the relation between correct unit rhombohedron of $NaNO_3$ arrangement and its cleavage rhombohedron. The bimolecular unit is the elongated cell. It crystallizes in rhombohedrons with almost the same angles as the unit (or cleavage of) rhombohedron of calcite $\left\{ (10\bar{1}1) \wedge (01\bar{1}1) \right\} = 73^{\circ}-30'$. It is isostructural and hemo morphus with calcite. Its space group is $R\,\bar{3}\,C$, with $a_{rh} = 6.3247$; $\alpha = 47^{\circ}-15'$, $a_o = 5.07$, $C_o = 16.81$ and $a_o : C_o$

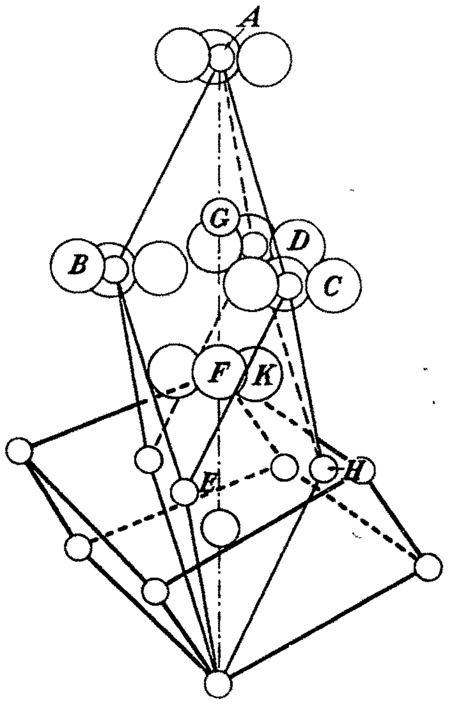

Fig. 1.1 A drawing showing the relation between correct unit rhombohedron of the sodium nitrate arrangement and its cleavage rhombohedron. The bimolecular unit is the elongated cell, the cleavage pseudocell is that outlined by thick lines. Small circles at the corners are nitrogen atoms. Big circles are oxygen atoms.

:: 1 : 3.316. The $NaNO_3$ structure is having a less planer structure compared to $CaCO_3$. The distance between central nitrogen atom to oxygen atom is 1.21 Å, while each side of equilateral triangle (made by oxygen atoms) has a length of 2.108 Å.

1.1.5 FORM AND HABIT

Usually massive granular form is available in natural $NaNO_3$. It is found with Darapskite with minor traces of various iodates, borates and chromates.

Artificial crystals, usually obtained are rhombohedrals $\{10\bar{1}1\}$. They are rarely observed with modifying faces. Habit variations in artificial crystals due to impurities in the crystallizing solutions are studied by France and Wolfe.[2] A growth study of synthetic large single crystals of $NaNO_3$ was done by Stober,[3] West[4] and F. Yamaguti.[5] Ca, Li, K and NH_4 go only in traces to replace Na atoms in $NaNO_3$ crystals.

1.1.6 TWINNING GLIDING AND PERCUSSION MARK

The phenomenon of twinning is observed in accordance with the following rules in $NaNO_3$ crystals,

(i) On $\{01\bar{1}2\}$ often elongated along the common rhombohedral edge ;

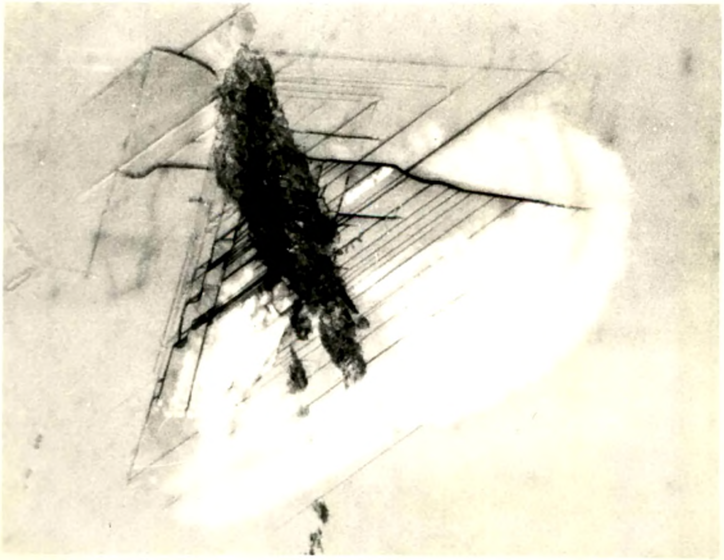

Fig. 1.2 Percussion mark on cleavage face of synthetic single crystal of sodium nitrate.

(ii) on $\{0001\}$ as penetration twin ;

(iii) on $\{02\bar{2}1\}$ sometimes as aggregates of three or six individuals,

(iv) on $\{10\bar{1}1\}$ rare.

It also exhibits twin-gliding with K_1 $\{10\bar{1}2\}$, K_2 $\{0\bar{1}11\}$ and Percussion figure similar to that on calcite. Percussion mark on cleavage face of $NaNO_3$ grown in this laboratory is shown in Fig. 1.2.

1.1.7 ORIENTED OVER-GROWTHS

Sodium nitrate readily forms over growth upon calcite (Finch and Whitmore).[6] The crystal axes of the substances are usually parallel. Its growth and orientation on muscovite (Mugge[1] 1902), on dolomite (Tschermark[1] 1882), on baryto - calcite (Krentz[1] 1909), on alkali halides (Royer and Heintze[1] 1937), on certain phenols (Willems[1] 1943) and also upon $NaNO_3$ rhombohedra are well known. (References marked 1 are quoted in 'The System of Minerology' Vol. II by Dana and Ford[1])

1.1.8 PROPERTIES OF SODIUM NITRATE CRYSTALS

For pure $NaNO_3$ crystals specific gravity is 2.267. It has perfect cleavage $\{10\bar{1}1\}$, cleavage along $\{10\bar{1}2\}$ and $\{0001\}$ are also reported. Its fracture is conchoidal but seldom observable. It is usually colourless and transparent or white when pure. The colour varies from colourless to reddish brown, gray and lemon yellow when tinted by impurities. It is uniaxial negative. Refractive index on cleavage is E' = 1.467. Birefringence $n_o - n_e = 0.251$ is due to the different polarization of oxygen atoms in different directions. However the refrective indices are smaller than those of calcite.

Hardness on Mho's scale is 1. $NaNO_3$ crystal undergo lattice distortion at temperature approaching λ-transition, there being less than 2% change in volume[7]. The transition takes place reversibly, over the range 150° to 275°C.[8] The $NaNO_3$ gradually changes from calcite structure to a closely similar one, still rhombohedral, in which nitrate ions are essentially (but not strictly) disposed at random between two possible orientations, α and β, differing by a 60° rotation about three fold axis[9]. Its melting point is 306.8°C and decomposes at 380°C. Its thermal conductivity is maximum along $\left[0001\right]$ direction. It is diamagnetic. The solubility of sodium nitrate in water is more a chemical property than a physical one because it is an endothermic process. 73 gm. of $NaNO_3$ gets dissolved in 100 cc. of distilled water at 0°C.

It is very soluble in ammonia, slightly soluble in glycerine and very slightly soluble in acetone.

1.1.9 USES

Sodium nitrate is used as an oxidizing agent in general and in particular in solid rocket propellants and fertilizer. At the time of second world war calcite was replaced by sodium nitrate in polarizing microscope for polarizing prism due to shortage of calcite. Since sodium nitrate is hygroscopic, precautions were taken to keep it free from moisture. However it could not completely replace the calcite crystals. It is used as a flux in general and in particular glass manufacturing process, as a refrigerant and also as a reagent in analytical chemistry. It is used in pyrotechnics, medicine, matches, dynamites, military explosives and gases, manufacture of sodium salts, nitrates, dyes, pharmaceuticals, food preservative, colour fixative for meats, enamel for pottery, modifying burring properties of tobacco etc. etc.

1.2 GENERAL INFORMATION ON CALCITE

1.2.1 INTRODUCTION

In the entire mineral kingdom, next to quattz no species are more abundant, wide spread or beautiful than calcite. The mineral by virtue of the size, abundance and perfection of its crystalline structure and its remarkable complexity of habit has attracted the attention of crystallographers and has played a prominent role in the history of minerology. There is such a vast literature on calcite that it is very difficult to give a brief account of it. However, a humble effort is made on these pages to present briefly information on some of its features. Mellore[10], Dana and Ford[11] and Rogers[11] have given a nice account of calcium carbonate (calcite).

1.2.2 OCCURRENCE

It occurs in nature in several localities and ranges in character from pure transparent single crystals to large conglomerate masses which are quite opaque. It occurs ; (i) in veins, cavities and amygdules, due to penetration of calcareous solutions, (ii) as a cellular tissue of many phanerogamia, e.g. cycadeae and cactaceae, (iii) as a rock forming minerals in the sedimentary cycles and in great thicknesses in relatively pure form as chalks, and lime stones, (iv) as a biogenic mineral forming lime stones, organisms such as mollyseas, branchiopads, Corals and orinoids contributing their shells or other hard parts, (v) as a diverse from, calcereous sinter or tufa or travertine ; the tophus of pling and lapis fiburatinus of pling and vitruvius and formation of stalactites and stalagmites in caves, (vi) as a paramorph after argonite. Calcite, a carbonate of divalent metal of calcium has a formula $CaCO_3$ (CaO lime 56.0% ; CO_2, carbon dioxide 44.0%). Natural calcite is very rarely pure calcium carbonate. Small quantities of Mg, Fe, Mn, Zn and Pb may be present replacing the calcium.

Calcite is the stable form of calcium carbonate at ordinary pressure and over a large temperature range. The metastable polymorphous are known such as aragonite and vaterite. The polymorphs change irreversibly to calcite on being heated. The occurrence of a form known as α - calcite (elatolite) stable at high temperature has been disproved.

Calcite by virtue of its relatively high chemical reactivity and ready solubility in carbonated water is very commonly found and replaced by or altered to other species. That is why it enters into a wide range of compositional variation through the substitution of other divalent cations for calcium.The limits of variations in the indices of refraction, specific gravity, unit cell dimensions and crystal angles accompnaying variation in composition are not yet fully established, especially in the polycomponent system.

1.2.3 CALCITE GROUP AND ITS STRUCTURE

The anhydrous carbonates include two distinct isomorphous groups, the calcite group and the aragonite group. The metallic elements present in the former are magnesium, iron, manganese, zinc and cobalt ; in the later are barium, strontium and lead. Calcium is common for both the groups. The calcite group is characterized by rhombhedral crystallization, perfect rhombohedral cleavage and the angle varying from 73° to 75°.

The crystal structure of calcite, one of the earliest studied by x-rays, was described by Bragg[12] in 1914. He later on derived the optical properties of both calcite and its polymorph aragonite in terms of the atomic structure. In fig. 1.3, calcium atoms are represented by black circles, carbon atoms by lined circles and oxygen atoms by black circles. The calcite lattice may be regarded as a deformed rock salt lattice. The later is stood on a diagonal (looked at from above in the figure) all the Na^+ ions replaced by Ca^{++} ions and all the Cl^- ions by CO_3^{--} ions,

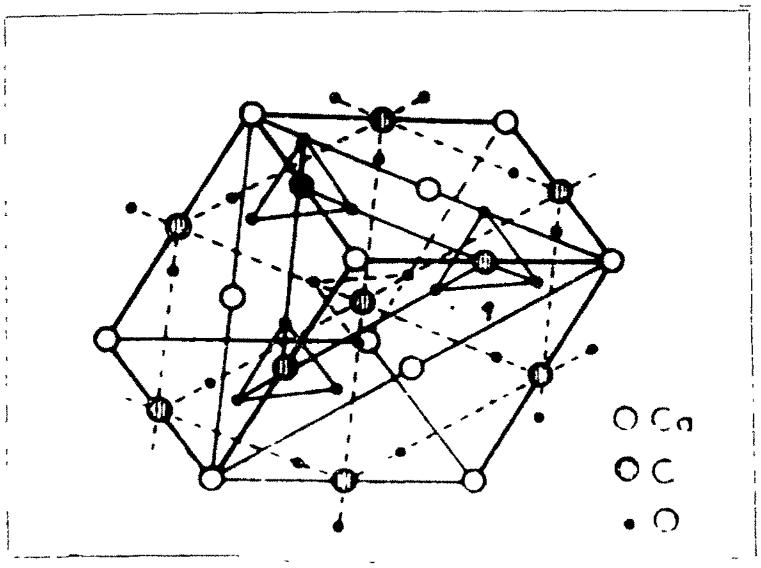

Fig. 1.3 The calcite lattice, with calcium atoms by black circles, carbon atoms by lined circles and oxygen atoms by small black circles.

consisting of central carbon atoms in a plane at right angles to diagonal (i.e. the plane of the paper). On account of the space occupied by three ions, the cube expands in a horizontal direction and forms the cleavage rhombohedral of calcite. Calcium and carbon atoms are spaced at equal intervals along the crystal axes. In contrast to other XO_3^{--} ions (e.g. NO_3^-, ClO_3^- etc.) the carbonate ions CO_3^{--} is having a planer structure. The distance between central carbon atom to oxygen atom is 1.23 A while each side of equilateral triangle (made by oxygen atoms) has a length of 2.13 A.

1.2.4 FORM AND HABIT

Calcite is found as well defined crystals (often large in size) in crystalline crusts and drushes, in cleavage masses, in various forms such as stalactitic, pisolitic and colitic in granular masses and sometimes in fibrous or lamellar forms.

Crystals show four distinct habits (i) rhombohedral (ii) prismatic (iii) scalenohedral and (iv) tabular. Calcite is typical example of the hexagonal scalenohedral class, embracing some of the finest, the largest and most abundant of all crystals. In number of forms and variety of their combinations, calcite is unsurpassed among minerals. Over 300 well established forms most of them scalenohedrons are known, the rhombohedral being very frequently the dominant form in the combinations. Calcite, quartz, apatite etc. are most remarkable for their outstanding size in the mineral kingdom. Special names have been given to the more peculiar habit of calcite ; for instance, there are so-called dog-tooth spar, nail-head spar and satin spar. It is fibrous variety with a silky lustre resembling the satin star variety of gypsum, the later is harder than the former. There are several varieties of minor importance which have been named after some admixture or the colour, use of locality and do not generally indicate important structural or chemical differences, for example, dolomite, calcite containing manganese carbonate is known as manganocalcite, ferro-calcite containing ferrous carbonate and calcite etc.

1.2.5 CLEAVAGE GLIDING AND TWINING

It has a perfect rhombohedral cleavage, a cleavage in three directions at oblique angles (74^{o}-55') to each other, and is susceptible to abrasion or scratching. Some crystals exhibit areas upto 0.2 mm x 0.2 mm free from cleavage lines, over such an area the crystals appear to have cleaved true to a single molecular plane.[13] The cleavage spacing between rhombohedral faces is 6.1 Å. The crystals cleave so readily that light blows will shatter them into fragments and they are soft enough to be readily scratched with a knife ; extreme care has to be exercised in handling them. There is often parting parallel to $\{0001\}$. Fracture is conchoidal but difficult to produce, since it is brittle.

Four twinning laws are known for calcite (i) Twin plane $\{0001\}$ as the composition surface. Re-entrant angles are about the equator of the crystal except when bound laterally by $\{10\bar{1}0\}$. The twinning then revealed by cleavage or by the apparent horizontal plane of symmetry. (ii) Twin plane $\{01\bar{1}2\}$ is very common with $\{01\bar{1}2\}$ as the composition face. This is often known as polysynthetic twinning with striations parallel to the long diagonal. (iii) Twin plane $\{10\bar{1}1\}$ is not common with composition surface $\{10\bar{1}1\}$. The twinned individuals have their axes nearly at right angles and also have a cleavage plane in common. (iv) Twin plane $\{02\bar{2}1\}$ is rare with composition plane $\{02\bar{2}1\}$.

1.2.6 PERCUSSION MARK

The results of the study of the impact of solid polished steel spheres on the optically polished surface (or cleavage) of calcite show that the general nature of the effects observed is a characteristic property of the crystal itself and is related both to the structure of the crystal and to the orientation of the face on which the impact occurs.

It is observed from the study that on either side of the area of contact between the impinging sphere and the crystal, two cleavages making an obtuse angle (102°) with each other developed and extended outwards from the edges of that area (Fig. 1.4). These cleavages are clearly visible on the face of the crystal and they sharply limit the area within which fracture develops. Another interesting feature is the appearance of a whole series of parallel lines outside the region equally inclined to the two sets of cleavages and may be explained as being due to glides occuring within the crystal along the direction of a rhombohedral edge.[14]

Percussion mark can also be observed by a sharp quick blow with a dull conical point on a calcite cleavage surface. It is helpful in determining the orientation of the crystal and etch marks on cleavage surface of calcite. The whole percussion figure with the point of impact as the vertex of the triangle formed

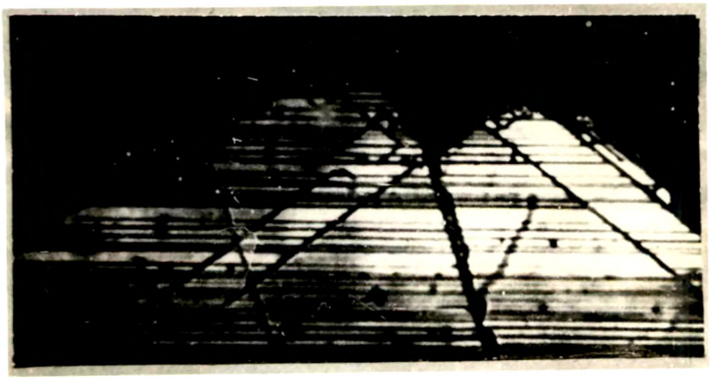

Fig. 1.4 Percussion mark on cleavage face of natural calcite crystal.

by two cleavages and the series of lines is oriented appositely with respect to the corner of the crystal, where the three obtuse angles meet. The line which is perpendicular to the series of parallel lines and passing through the vertex of the triangle has direction [110] , which is also the line of symmetry for the cleavage surface and percussion mark. The percussion figures are very important in the present studies, since with reference to them the orientation of etch pits and their boundries are determined.

1.2.7 PROPERTIES OF CALCITE CRYSTALS

For pure calcite specific gravity is 2.7102 (± 0.0002) at 20°C, but varies somewhat widely in impure forms as in those containing iron, manganese etc. It is usually colourless and transparent or white when pure. The colour varies from white to various pale shades of gray, red, green, blue, violet, yellow; also brown and black when impure. It may be translucent or opaque due to isomorphous substitution. Lustre is vitreous to subvitreous to earthy. Many specimens are fluorescent and often show phosphorescence upon heating and other luminescent properties upon being exposed to sunlight or radium emanations. Calcite is optically negative and birefringence is very high. Refractive indices for sodium D line are $\mu_o = 1.658$

and μ_e= 1.486. Birefringence is due to the different polarization of oxygen atoms in different directions. Several workers have determined birefringence of calcite at several visible wavelengths and at different temperatures.[15]

Hardness on Mho's scale is 3 but varying somewhat on different planes and in different directions thereon, relatively soft on $\{0001\}$ and relatively hard on $\{10\bar{1}0\}$. Calcite decomposes into calcium oxide and carbon dioxide at 850°C and it melts near 1289°C under a pressure of 110 atmospheres.

The solubility of calcite in water is more a chemical property than a physical one. In pure water it is very sparingly soluble, but in water containing carbon dioxide it dissolves to some extent (1.56 gm at 0°C in a litre of solution saturated by carbon dioxide at one atmosphere) and appears to form calcium bicarbonate. Its solubility in different solvents has attracted much attention on account of the bearing of the results on geological processes and on the nature of the soil-solution.

Calcite and other forms of calcium carbonate can always be easily recognised by their easy solubility with brisk effervescence in cold diluted acids, the properties possessed by no other common minerals resembling calcite.

1.2.8 USES

Finest variety of calcite, known as iceland spar is used in optical apparatus especially for the polinizing prisms of the polarizing microscope. Limestone which is more or less an impure form of calcium carbonate has tremendous industrial uses and surpasses all other minerals in the number and diversity of its uses. An excellent account on calcium carbonate and its manifold uses is given by Searle[16] and a physico-chemical survey of high grade Indian limestones is done by Bijawat and Sastri.[17] In the manufacture of mortars, cements, as a building and ornamental material calcite is used. It is also used as a fertilizer in the form of chalk.

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CHAPTER - II

EXPERIMENTAL TECHNIQUES

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EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

The various experimental techniques employed during course of this work are briefly described here. For the quantitative and qualitative measurements of features on the crystal surfaces, the high resolution technique is used. Scanning electron microscope is also used for greater detail and accuracy. To study plastic deformation and other related phenomena the static indentation technique is employed. The diamond pyramidal indenters of different geometry are used with VERTIVAL Incident Light Microscope. The crystals of sodium nitrate are grown from solution and from melt. Besides etch method, electrolytic conductivity bridge, semi-milro balance and heating devices used for present study are also described in this chapter.

The techniques mentioned above are well-discussed in several standard text books (e.g. Gillman[1], Mott[2], Venables[3], Martin and Johnson[4], Clark[5], Tolansky[6]). Hence only a brief discription together with their salient features will be given here.

2.2 VERTIVAL INCIDENT LIGHT MICROSCOPE (CZ)

The VERTIVAL microscope manufactured by Carl Zeiss Jena is one of the best and sophisticated instruments amongst the metallurgical microscopes. It can be used for different types of illuminations. Its utility is enhanced

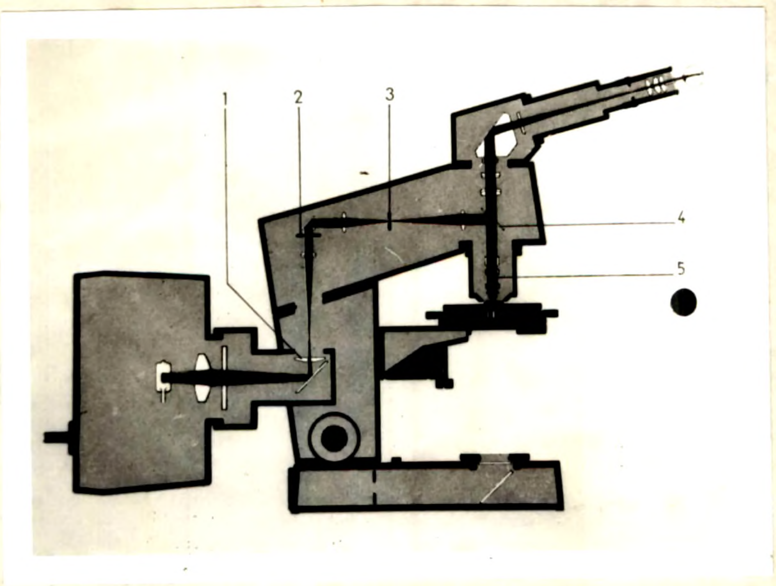

Fig. 2.1 Ray diagram for bright field.

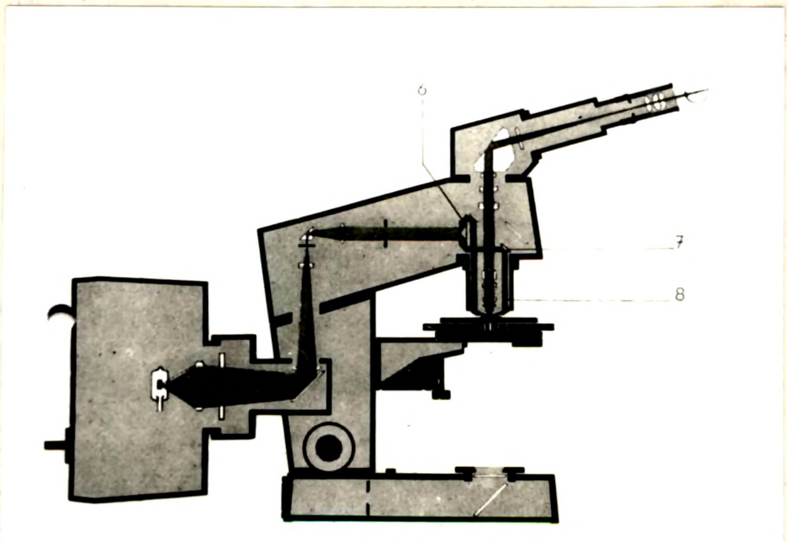

Fig. 2.2 Ray diagram for dark field.

by providing different attachments which can be fitted to this microscope such as hardness testing unit, polarising 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 course motion brake and illuminating unit incorporating bright field and dark field, for the coordination of concave mirror condensers etc. Excellent account of the above is given in the instruction manual supplied by the manufacturer. The basic unit of microscope consists of (i) the illuminating system, (ii) the stage for placing the sample, (iii) the 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 2.1 and 2.2. 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 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 in a clockwise direction until the desired smoothness has been attained.

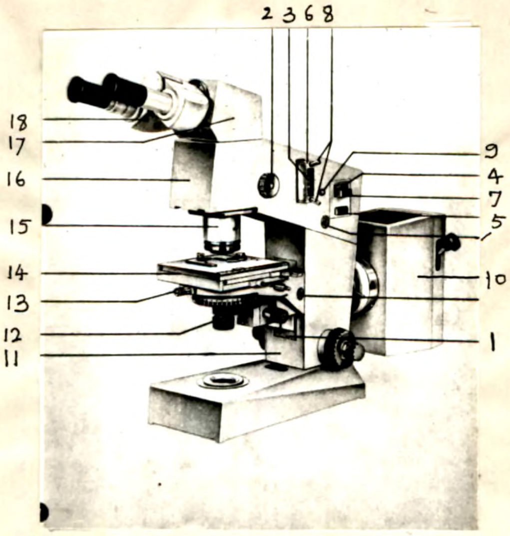

Fig. 2.3 Vertival Incident Light Microscope

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

(b) Adjustment of the illuminating equipment

Having switched on the lamp, set switching knob (2) to bright field (see para d) and on opening diaphragms (3 and 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 side screws 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 centring screws (5).

(c) Coordination of concave mirror condensers

The coordination 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 angular tube (1.6X) and monocular or binocular (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. 2.3)

For carrying out examinations in bright field the switching knob (2) has to be turned untill 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 allignment. A green filter, an attenuation filter or a froasted glass may be introduced optionally or in a combined form into the filter slide (7). This slide is provided with a free passage. Filter and shutter slides have to click indistinctly. The luminous field diaphragm is centred by actuating the two centring screws (8) and the aperture diaphragm by making use of socket wrenches to be put on to the two centring screws (9).

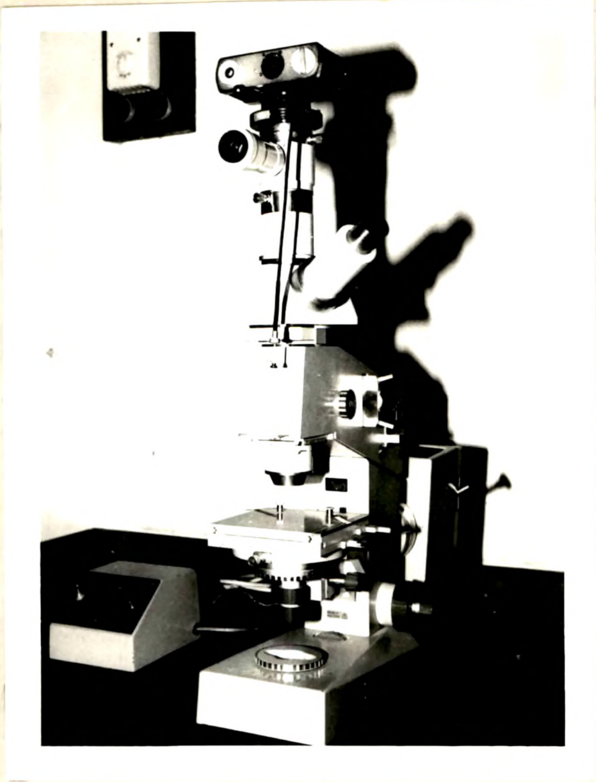

Fig. 2.4 Camera attachment on microscope

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. 2.3)

For investigations in the dark field the objective corresponding to desired magnification has to be fitted with the concave mirror condenser coordinated 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 and 4).

(f) Camera attachment (Fig. 2.4)

For taking photomicrographs of samples, camera is attached to the microscope. The arrangement is shown in fig. 2.4. The advantage of this method is that it is possible to observe the sample while taking photographs. Exposure times can be automatically controlled.

2.2.1 Indentation technique

mhp 160 microhardness tester : (Fig. 2.5)

The indenting device (19) and the threaded socket for objective (20) are mounted on a common carraige, which can be moved to and fro laterally by handle (21) in the

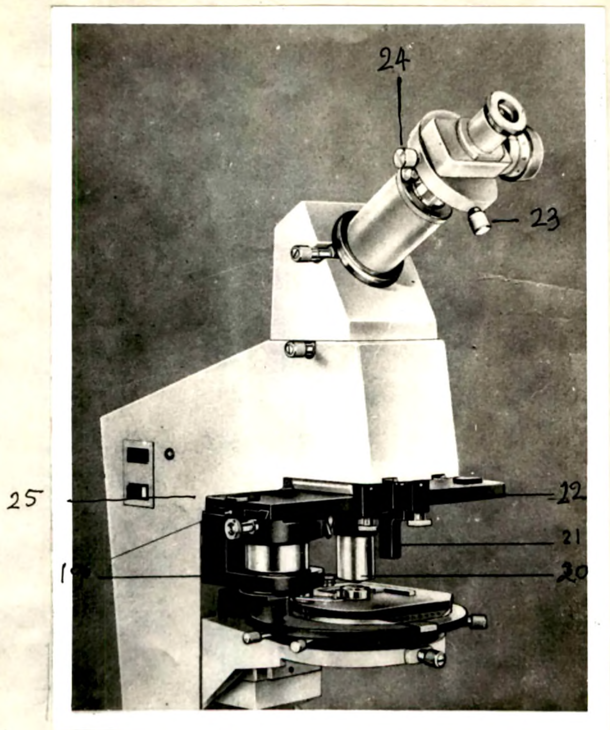

Fig. 2.5 Indentation technique

19. Indentation device
20. Objective
21. Handle
22. Slide
23. Centring screws
24. Centring screws
25. Centring screws
26. Centring screws

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 fitment is attached to the upper surface of the slide for mounting the microhardness tester in the corresponding microscope. The indenter device is suspended from two springs, so that it is rather sensitive to vibrations, which are manifested by continuous or intermittent swings of the index line on the force scale. If the vibrations exceed the tolerable level or (what is rarely the case) have a frequency that is in reasonance 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 effect the hardness readings considerably.

Various diamond pyramidal indenters may be used with mhp 160 micro hardness tester. Regular four - sided Vickers indenter and the knoop indenter with rhombic base are employed in the present investigation. They are kept in a 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 a closed case when not in use to avoid dust settling 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 centring 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 feature or intersection of centring cross section coincides with eye-piece cross.

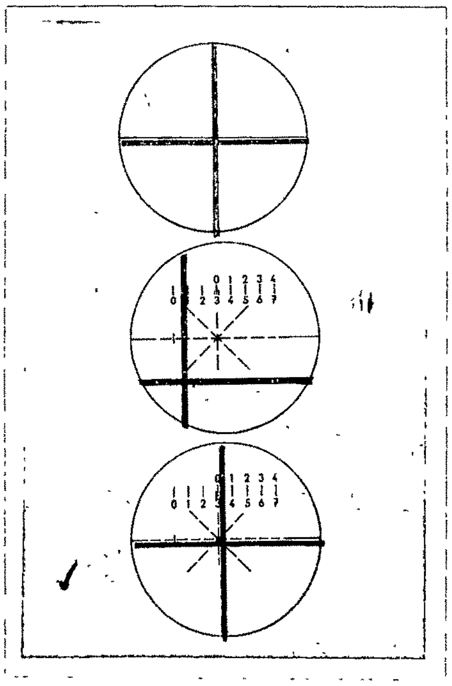

Fig. 2.6 Zero position of cross wire on graticule of micrometer eyepiece.

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

(5) By turning the centring screws (23 and 24) bring the apex of fixed (left measuring arm of eye-piece screw micrometer to coincide with the striking feature of object or centring cross. Both measuring arm form a cross (zero position). (Fig. 2.6).

(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 focus on to specimen.

(9) Centre the objective by turning setting screws (25 and 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 eye-piece (Fig. 2.6).

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

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

(12) Observe the horizontal bright index line of the load

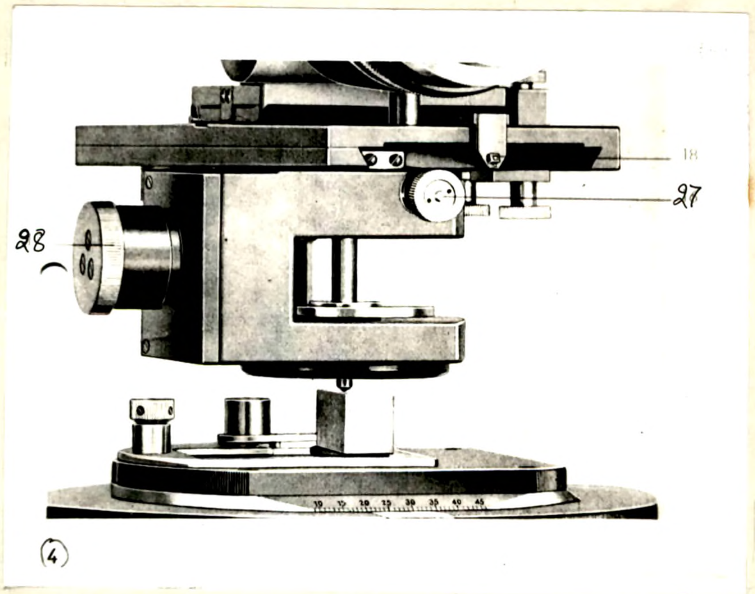

Fig. 2.7 Indentation technique

27. Knurled knob
28. Rear knurled knob

5

indicator in the eyepiece. If it is not seen, turn the rear knurled knob (28, Fig. 2.3) on microhardness tester until it is seen.

(13) Focus 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.

(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 the original reference line.

(20) Turn fine motion knob in 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.

2.3 SCANNING ELECTRON MICROSCOPY

2.3.1 INTRODUCTION

By 1960 combination of optical and electron microscopy covered large range of magnification and resolution needed to study super-atomic world ; but there were still important limitations in their use, notably the limited depth of focus of the optical microscope and the fact that the ordinary electron microscope, which was not much used in reflection, was almost entirely restricted to the examination of very thin specimens, requiring special preparation. Scanning electron microscope has filled these gaps, enabling detailed microtopographical study of crystal surfaces.

2.3.2 MICROSCOPE

The essential features of the scanning electron microscope are as follows :

(1) an electron source

(2) a means of focusing a tiny spot of electrons from the source on the specimen,

(3) a means of scanning the spot across the specimen,

(4) a means of detecting the response from the specimen,

(5) a display system, capable of being scanned in register with incident scan,

(6) a means of transmitting the response from the specimen to the display system.

Fig. 2.9 shows the commonest mode of use in which the electrons scattered by the specimen collected as the response of the specimen.

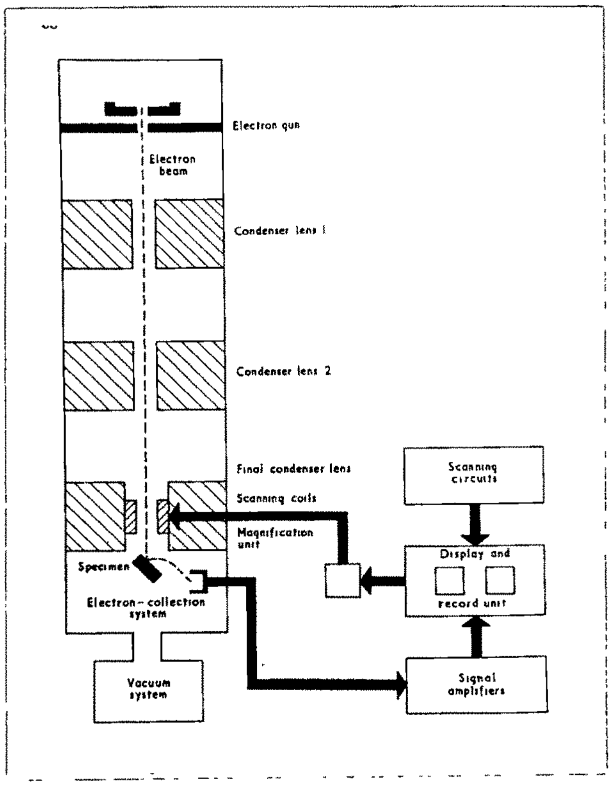

Fig. 2.8 Schematic diagram of scanning electron microscope (SEM).

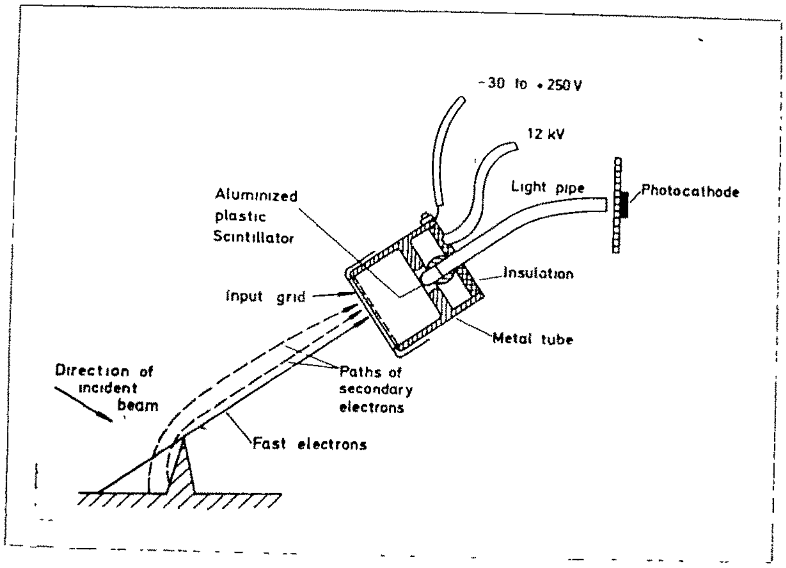

Fig. 2.9 Diagram showing scattering of electrons by the specimen in SEM.

For the present work ISI 100 Scanning Electron Microscope (SEM) was employed (Fig. 2.10). Further on the left there is column of SEM (Fig. 2.10). It consists of source (the electron gun), the lens system collector and mechanical stage. The display system consists of the cathode ray tubes along with photographic recording with the usual contrast and brilliance controls found on a television receiver. The electron probe size is correlated with magnification attainable so that the instrument resolution becomes related to that attainable with the human eye. The vacuum system must produce vacuum of about 10^{-5} to 10^{-6} torr residuel pressure. The vacuum is produced by a combination of rotary and diffusion pumps with suitable baffling to prevent oil streaming into electron optical column.

2.3.3 SPECIMEN PREPARATION

Conducting samples usually need nothing more than cutting to an appropriate size, sticking to a convenient metal mount making sure there is a good electrical conduction between the specimen and the mount. The size of the sample taken varies widely with the model of SEM used. The type of glue should be one that does not seriously outgas in the vacuum used in the instrument, is prepared easily and dries quickly. Useful technique is to mount specimen with a double sided adhesive tape (twinstik) making sure that

Fig. 2.10 ISI Scanning Electron Microscope.

Fig. 2.11 Advance Sputter Coater.

there is a good conduction from the specimen by using Aquadag or any silver glue.

Unfortunately, some samples, mainly nonconductive ones, do not give a clear picture when prepared in the above manner and viewed under normal conditions in the microscope. The four obstacles to clear pictures which necessiate more complicated preparation procedures are electron emission, charging beam damage and vacuum damage.

The application of a conducting layer of carbon (Chatterji et al.,[7]) or of metal of moderate thickness is the most popular method of suppressing charging and increasing electron emission but, while simple to perform, has a number of potential drawbacks. The purpose of coating is to put on a uniform covering of conducting material, so that the surface of the coating is, as nearly as possible, an exact replica of the surface of the underlying material. For scanning electron microscopy, the conducting material may be deposited by sputtering on the sample surface under high vacuum. The advance sputter coater (Fig. 2.11) was used.

2.3.4 ADVANCE SPUTTER COATER

For the present study samples have been prepared with different coating materials like carbon, gold or deposition of carbon film and gold film one over the other. The thickness of the coating layer must be adjusted in such a manner that adequate emission of electrons from all major and minortopographical features could be obtained. This will highlight the topography. It was found from the SEM study of a large number of samples (freshly cleaved and /or etched surfaces of calcite coated by different materials (carbon and gold and/or deposition of multilayers of carbon and gold or of gold and carbon) and optical study of the cleavage counter part (vergin and/or etched) that gold film was suitable and that its thickness should be less than 80 A for SEM topographical study.

2.4 ETCH METHOD

2.4.1 Chemical etching

This method consists of carefully preparing crystal surfaces and solutions of desired composition and concentration and 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 running solvent such as water which does not affect the crystal surface chemically. 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.

Big blocks of crystal were cleaved in a usual way i.e. by keeping a sharp razor along cleavage direction and then giving a sharp blow. Everytime freshly cleaved crystal surfaces were used.

2.4.1.1 Preparation of solution

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

(i) Percentage by volume : Suppose x c.c. of liquid X are poured in y c.c. of liquid Y such that $x + y = 100$ then it is known as x % liquid X.

e.g. (1) If 10 c.c. of Formic acid poured in 90 cc. of acetic acid to form a solution of 100 c.c., then it is 10% formic acid solution in acetic acid.

(ii) Molarity : The number of gram molecules of a solute dissolved in one litre of the solution is called molar concentration or molar strength. Suppose that 'X' grams of solute having molecular weight 'W' are dissolved in a solvent to make total volume 'Y' litres then the molarity M of the solution will be,

$$M = X/W \times 1/Y$$

e.g. (1) 80 gm. of NaOH pellets are dissolved in 100 cc. of distilled water then molarity of solution is given by(Mol.wt. of NaOH = 40 gm/mole).

$$M = 800/40 \times 1/1$$

$$= 20$$

(iii) Normality : This is most widely used unit of concentration. Normality of an acid is given by

$$\text{Normality} = \frac{\text{gms per litre}}{\text{Eq.wt.}}$$

$$= \frac{\text{gms. per litre}}{\text{Mol.wt./basicity}}$$

$$\text{or} \quad \frac{\text{Vol. per litre x density x basicity}}{\text{Mol. wt.}}$$

If percentage purity of an acid is given as p %, then

$$N = \frac{V \times d \times b \times p}{M \times 100}$$

where N = Normality

V = Volume per litre

d = density of an acid

b = basicity of an acid

M = Molecular wt. of an acid

p = percentage purity of an acid

e.g. (1) when 60 c.c. of acetic acid ($M = 60.05$; $d = 1.049$; $p = 99.8\%$) are dissolved in 40 c.c. of distilled water, then

$$N = \frac{V \times d \times b \times p}{M \times 100}$$

$$= \frac{60 \times 1.049 \times 99.8}{60.05 \times 100}$$

$$= 1.044 \qquad \text{(where } b = 1\text{)}$$

(ii) When 40 grams of NaOH (Mol. wt. 40) pellets dissolved in 100 c.c. of water ;

$$\text{Normality } N = \frac{\text{gms. per litre}}{\text{Eq. Wt.}}$$

$$= \frac{\text{gms. per litre}}{\text{Mol.wt.}}$$

$$= \frac{400 \times 1}{40}$$

$$= 10$$

(iv) <u>Mole fraction (m.f.)</u> : Mole fraction is defined as

$$\text{m.f.} = \frac{\text{Weight of solute/Mol.wt. of solute}}{\text{Weight of solvent/Mol.wt. of solute}}$$

Mole fraction multiplied by 100 is called mole percent e.g. (1) 120 gms. of KOH (mol.wt. = 56) when dissolved in 100 c.c. water.

$$\text{m.f.} = \frac{\text{Weight of KOH/Mol.wt. of KOH}}{\text{Weight of Water/Mol. wt. of water}}$$

$$= \frac{120/56}{100/18}$$

$$= 0.3857$$

and mole percent = 0.3857 x 100%

= 38.57%

2.4.1.2 Etching at different temperatures

The etching was normally carried out in two different ways, depending upon the temperature of etching viz. etching (a) at room temperature and (b) at high and low temperature.

(a) Etching at room temperature :

Since the rate of stirring of etching solution noticeably affects the etch pattern at room temperature, etching was carried out under the condition of static etching (No stirring). In static or still etching, the motion of etchant relative to the crystal being etched is absent.

(b) Etching at high and low temperatures :

Chemical etching can be done at high temperature to get quick reaction between the etchant and a crystal surface. High temperature etching alters the normal rate of etching at room temperature. In this method etchant is therefore kept in an incubator or a muffle furnace or in water-bath (depending upon the etching temperature) for obtaining the required temperature.

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At low temperatures (ice temperature and below), the etching work was carried out in a container containing etchant in a beaker which was placed in a container or thermoflask to contain ice or ice-water or dry ice or liquid air. Low temperature etching reduces the etching rate. The washed and dried crystal surfaces were optically studied by using CZ VERTIVAL microscope. The length of etch pit along [110] was measured using filar micrometer eyepiece. The rate of surface dissolution is measured using semi-microbalance described in art 2.5 of this chapter.

2.4.2 Thermal etching

When crystal cleavages are thermaly treated in air, vacuum or any other medium which does not react chemically, thermal pits of regular geometry are usually produced.

Thermal etching was carried out on calcite cleavages. The freshly cleaved sample was kept in crucible in furnace described in this chapter Art. 2.6(a), and slowly the temperature was raised to obtain to desired one in a period of two hours. The elevated temperature was kept constant for few hrs. and the temperature was lowered to room temperature. The optical examination of crystal surface reveals the thermal pits.

2.5 SEMI-MICRO BALANCE

The balance utilizes the principle of weighing by substitution and the constancy of sensitibilities over all loads. The later feature distinguishes it from ordinary beam balance where the sensitivity depends on the load, i.e. it changes with the load in a way which reflects the relative positions of the three knife edges viz. left, central and right on which the beam rests. Further in contrast to the ordinary balance the present one is fully loaded when used.

The balance consists of three parts :

(i) Illumination system,

(ii) Optical system and

(iii) Weighing system.

Procedure for weighing a specimen

(1) Determine the approximate weight of the given specimen by ordinary beam balance.

(2) Put the specimen on the pan and close the balance to avoid effect of vibrations due to air.

(3) Switch on A.C. Mains.

(4) Adjust the approximate known weight by moving knobs 1,2 and 3 (fig. 2.12).

Fig. 2.12 Semi micro balance

1. Knob giving weights in multiples of 10 gms.
2. Knob giving weights in multiples of 1 gm.
3. Knob giving weights in multiples of 0.1 gm.
4. Knob for adjusting 4th and 5th digit after decimal point.
5. Knob to make pan free; W_1 & W_2 - scale windows.

(5) Make the pan free by turning knob 5 anticlockwise.

(6) Scale will be seen in window W_1. Let it become steady.

(7) Turn the knob 4 such that marked black line is seen on the scale.

(8) Note the reading in the following way :

  (a) Knob 1 indicates scale reading which corresponds to weight in multiples of 10 gm.

  (b) Knob 2 indicates scale reading which corresponds to weight in multiples of 1 gm.

  (c) Knob 3 indicates scale reading which corresponds to weight in multiples of 0.1 gm.

  (d) Scale seen in window W_1 corresponds to 2nd and 3rd digits after decimal point.

  (e) Scale seen in window W_2 corresponds to 4th and 5th digits after decimal point.

(9) Turn the knob 5 clockwise to half-way position such that the light is not seen in the window W_1. This operation locks the pan.

(10) Open the glass shutter.

(11) Take out the sample carefully.

(12) Switch off the A.C. Mains.

Note : The balance is highly sensitive to jerks, shocks and vibrations. Hence adequate precautions must be taken to avoid this. Some of them are as under :

(1) Operate the balance with care.

(2) Do not touch the table carrying the balance.

(3) Rotate knob slowly and gently.

(4) After putting a specimen on the pan, close the glass shutter.

(5) This shutter should be opened after completing the entire operation for weighing.

2.6 FURNACE, OVEN, INCUBATOR AND WATER-BATH

(a) FURNACE (Fig. 2.13) (Tempo Electric Co., Bombay)

A cylindrical crucible type furnace having vertical temperature gradient was employed in the present work.

It is thermally regulated. The maximum temperature which can be obtained in it is 1200°C. It consists of (i) heating element, a helix wound between refractory material with lead outs and connections in the rear, (ii) temperature regulator, comprising and energy regulator unit, (iii) temperature indicator in the form of a thermoelectric pyrometer and (iv) safety devices.

Energy regulator unit (dial) is calibrated in terms

Fig. 2.13 Vertical temperature gradient crucible furnace.

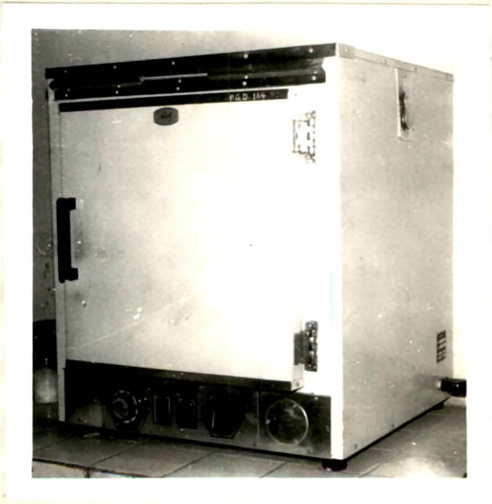

Fig. 2.14 Oven.

of temperatures so that the desired temperature can be obtained and maintained constant. The working space in the furnace is with dimension

Inner dimeter = 10 cm.
Height = 17 cm.

and with covering door for protective atmosphere. The accuracy of the temperature with the stabilized power supply is ± 3°C for long period of time.

(b) OVEN (Fig. 2.14)

A cubical oven used for study is manufactured by National Scientific Works, India. It consists of (i) heating element at the base, covering the base area for 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 at top portion and bent stem leading out of the oven.

Energy regulator unit (dial) is calibrated in terms of temperatures so that the desired temperature can be obtained and maintained constant for long period of time. The range of temperature is 0° to 250°C. The stabilized power is used to obtain temperature variations of ± 1°C. The working space is of dimension 20 inch x 20 inch x 20 inch.

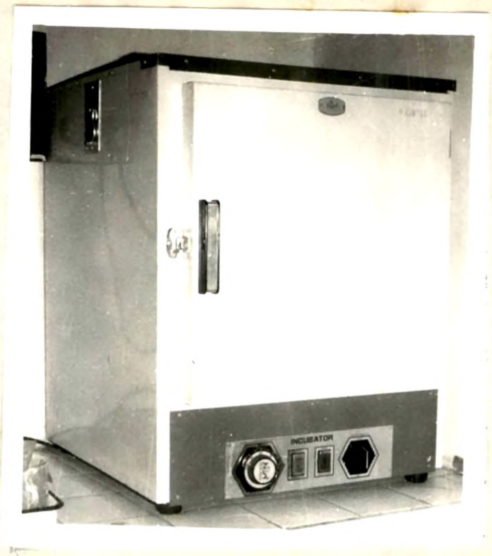

Fig. 2.15 Incubator

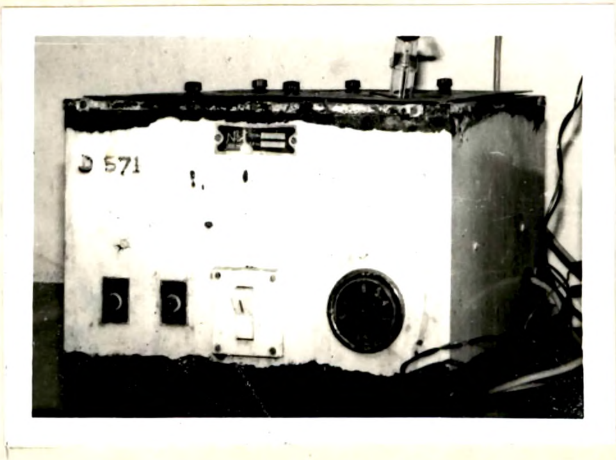

Fig. 2.16 Water-bath.

(c) INCUBATOR (Fig. 2.15)

A cubical incubator was employed for crystal growth from solution. Incubator operates on same principle as that of the oven described above and is supplied by National Scientific Works, India. The range of temperature is 0° to $100^{\circ}C$. Accuracy of temperature is $\pm 0.5^{\circ}C$. Temperature could be maintained constant for long periods.

(d) WATER-BATH (Fig. 2.16)

Thermostatically controlled water-bath manufactured by National Scientific Works, India was employed for etching the crystal cleavages. The water-bath consists of (i) U-shaped immersion heater of 1000 Watts and (ii) temperature regulator comprising of energy regulator unit with indicating lamps and temperature sensing device (thermocouple) connected at the centre of bath.

Energy regulator unit (dial) is calibrated in terms of temperatures so that the desired temperature can be obtained and maintained constant. A mercury thermometer was employed to read temperature with least count $0.1^{\circ}C$. The accuracy of the temperature is $\pm 0.5^{\circ}C$. The water-bath has cover with six circular holes of diameter 9.0 cm. and each hole could be covered with lids of smaller sizes. The bath is electrically insulated by glass wool in the walls and base.

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2.7 DETERMINATION OF ELECTROLYTIC CONDUCTIVITY

2.7.1 Introduction

Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. Specific conductance k is defined as the reciprocal of resistance in ohms (resistance offered by 1 cm. cube of the liquid at a specified temperature). For a more general case of conductance of a 'column' of area A and separation of the specific conductance,

$$K = \frac{\ell}{A} \times \frac{1}{R}$$

where R is the resistance of the solution. The ratio ℓ/A is termed cell constant. Unit of specific conductance is Mho per cm. To avoid inconvenient value in Mho per cm. of specific conductance, it is multiplied by 10^6 and is represented in micro mhos per cm.

Equivalent conductance is defined as the conductivity of a slab of solution 1 cm. thick and a sufficient breadth and length to hold one equivalent of electrolyte. The equivalent conductance is related to specific conductance by expression

$$K = C \lambda / 1000 ,$$

where C is concentration of the solution in gm. equivalent per litre and λ the ion velocity.

In electrolytic conductance current is carried through the solution by the movement of massive ions (rather than electrons) which act as a conductor. The specific conductance of a solution therefore increases with concentration and velocity of ions. Both positive and negative ions will share in carrying the current each moving towards the oppositely charged electrodes. Equation for conductance of each species

$$K = (C/1000) (\overset{+}{\lambda} + \overset{-}{\lambda})$$

only at large dilution the ionic conductance is known preciesly. In the present work electrolytic solutions for measuring electrolytic conductivity are etchants for delineating dislocations ending on a crystal surface. They are of different concentrations and are at different temperatures.

2.7.2 Wheatstone net

The resistance of a conductor is measured by employing either a potentiometer method or a wheatstone bridge arrangement. The second method is normally used. The passage of a direct current through an electrolytic conductor (liquid or solution) produces polarisation. This increases its resistance. A continued passage of current through such a liquid conductor creates decomposition which causes a change in the resistance due to alteration of the concentration of the electrolyte. These effects are avoided or reduced to a negligible amount by using alternating current. This is achieved by using small, rapidly changing alternating current and by employing identical electrodes of fairly large area. Thus the conventional wheatstone net is modified by employing an alternating source of emf, say output of an induction coil giving a low emf in place of D.C. source, e.g. battery and by using a telephone (or head-phone or a null detector) in place of galvanometer as a detector. Further the self inductance should be very small. This is achieved by a wire bridge instead of a post office box. This modified wheatstone bridge is shown in Fig. 2.17. Stretched wire AB is connected to an alternating source of emf e. T is telephone or head-phone and R is an adjustable resistance whereas V is a vessel containing electrodes and a known quantity of electrolyte (liquid or solution) of resistance Rx under consideration. For taking measurements at different high temperatures the vessel with electrodes and electrolyte is placed in a thermostatically controlled water bath. R is adjusted so that a point P is obtained near the centre of the bridge wire such that the sound in the telephone is entirely cut out or reduced to a minimum. When the usual wheatstone result is applied,

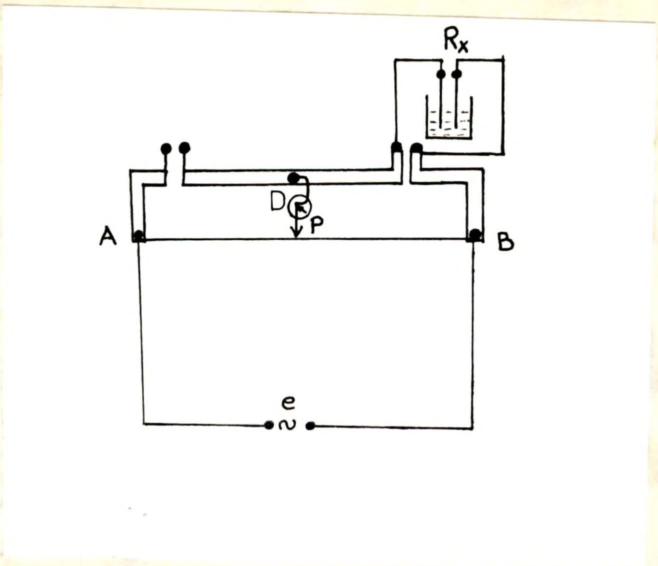

Fig. 2.17 Wheatstone net.

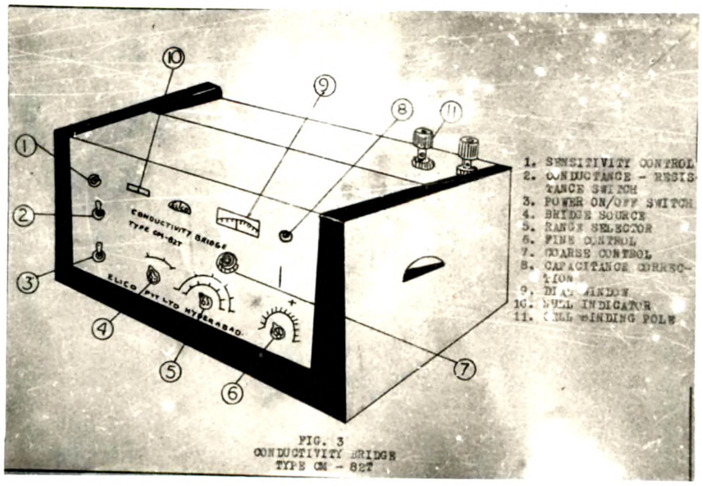

Fig. 2.18 Elico Conductivity Bridge.

$$\frac{R}{Rx} = \frac{AP}{PB}$$

$$\text{or} \quad R_x = R \cdot \frac{PB}{AP} \qquad \ldots (2.1)$$

The specific conductivity of the electrolyte of resistance R_x can be obtained by using the formula

$$K = \frac{\ell}{A} \times \frac{1}{R_x} \quad \text{mho - cm}^{-1} \qquad \ldots (2.2)$$

The value of ℓ/A , cell constant depending upon dimensions of the cell (vessel). It is obtained by finding Rx for a liquid of known specific conductance.

2.7.3 Conductivity measuring bridge

The 'Elico Conductivity Bridge ' model CM-82 T, a compact and versatile unit (fig. 2.18) was used for present study. It works on the principle of wheatstone bridge, which is slightly modified (fig. 2.19) as mentioned above. Excellent account of this is given in 'operating manual' of the bridge supplied by 'Elico Pvt. Ltd., HYDERABAD, INDIA. A typical conductivity measuring system consists of an A.C. source wheatstone bridge, electrodes or conductivity cell and a Null indicating device. Such a system is shown in fig. 2.18.

The null indicating device, sensitive D.C. Ammeter, which detects over an A.C. voltage sensing device. Condition of balance is indicated by no current flow through the null indicator (10) in Fig. 2.18. One advantage of using centre zero meter and phase deflecting network is to know whether the conductance of the sample solution is more or less than the selected range. The bridge circuit can be fed either at 50 C/s mains frequency voltage for electrolyte having low conduction or a suitable voltage at 1000 C/s for liquids of high conductivity. In both cases wheatstone net is supplied by alternating voltage, V. The bridge is connected to mains supply viz. 230 V, 50 C/s by screen cables.

The bridge is for determining and comparing specific resistances and conductivities of aqueous solutions with wide range of conductivity cells. The measurement of ohmic resistances can be over a wide range, namely from 0.1 ohm to 10^6 ohm in seven stages, multiple of 10. The conductance measurement are made in range from 0.1 micro mho to 1 mho. Absolute error including reading error varies with the range and region of the scale as mentioned below :

± 3% in 0.1 Mho to 1 Micro Mho

± 5% in 1 Mho to 0.1 Mho and

1 Micro Mho to 0.1 Micro Mho

The various controls of the bridge indicated in Fig. 2.18 are as follows :

Sensitivity control : (1) varies the sensitivity of the null detective amplifier. This control should be set at midway between maximum and minimum, at the time of obtaining rough balance and then adjusted for sharp balance.

Resistance - conductance Switch : (2) This allows selection of either the resistance or conductance as required.

ON-OFF Switch : (3) By throwing this switch up the instrument is switched ON :

Bridge Source Selectror : (4) This allows selection of source frequency either 50 Hz or 1000 Hz.

Range Switch : (5) Range switch is a seven position rotary switch.

Fine Balance : (6) A fine balance is obtained and full rotation corresponds to -0.1 to + 0.1. This reading is to be added or substracted from main dial reading to obtain the final value.

Dial knob : (7) By rotating this knob the bridge is balanced nearest to 0.1 division marking on dial.

Capacitive correction : (8) This corrects the reactive components in the circuit.

Dial : (9) The graduated dial is divided into 110 equal divisions (from 0.5 to 10.5) of 0.1, each division, representing conductance or resistance as the case may be.

Null Indicator : (10) It is a centre zero null indicating meter. If the resistance range selected is low the pointer deflects towards green, if the range is high it deflects towards red. At balance the point is in mid way.

Cell connections : (11) The two terminals on top of the instrument are to connect the conductivity cell to the instrument.

A fuse and earth terminals are provided at the rear of the instrument.

2.7.4 Measurement of conductivity

An experimental set up for measuring conductivity of a given solution is shown in (fig. 2.20). For efficient use of the bridge it is imperative to proceed in the following way :

(1) Plug in the instrument to mains connect rear terminal to earth.

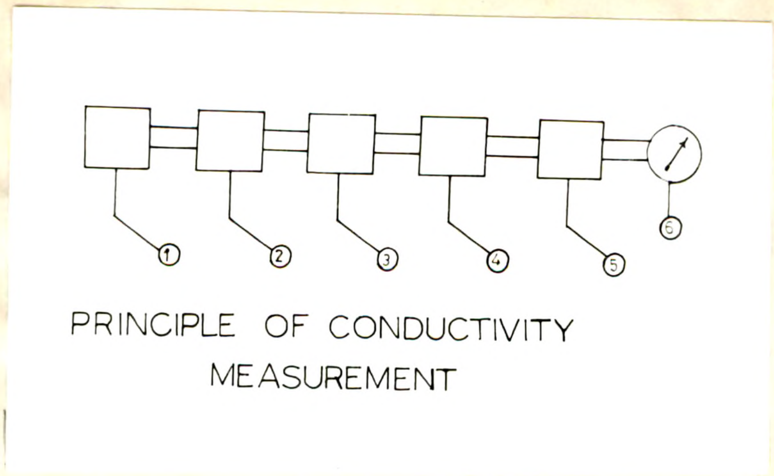

Fig. 2.19
1. **A.C. Input**
2. **Bridge of C.M. 82**
3. **Input Buffer**
4. **A.C. Amplifier**
5. **Detector**
6. **Indicator**

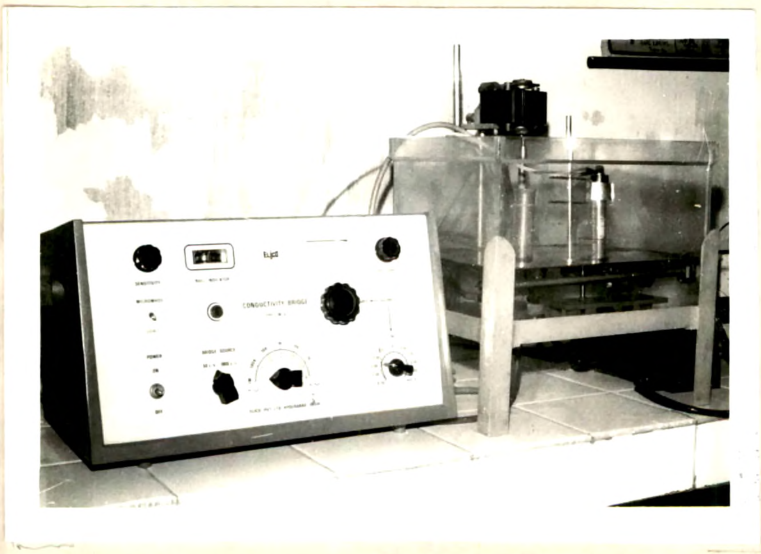

Fig. 2.20 Experimental set up of measurement of electrolytic conductivity of sodium hydroxide solutions along with water-bath.

(2) Keep the sensitivity control roughly mid-way between maximum and minimum.

(3) Take a clean conductivity cell and connect it to two terminals of the instrument at top. (Take the sample solution to the measured in a clean beaker) Place the cell in the beaker. Put the beaker with cell in a thermostatically constant temperature bath. Ensure that the platinum electrode plates of the cell are completely immersed.

(4) Select the resistance or conductance switch as the case may be.

(5) 'Switch On' the instrument, pointer in null indicator deflects in red or green region.

(6) If the pointer deflects towards red increase the range till it deflects towards null point mark.

(7) Search for coarse balance by rotating the coarse balance knob.

(8) Increase the sensitivity and obtain fine balance by adjusting fine balance control knob till balance is obtained.

(9) Fine balance indication should be added or substracted from main dial reading. The resulting dial reading

in range selected, gives the resistance or conductance of the unknown solution.

(10) To obtain the conductance of the solution, multiply the conductance by cell constant, supplied with each cell.

Example : The 0.01 N solution of KCl when measured on the bridge with a cell constant of 0.5 micro mho per cm. The following readings are obtained.

Range Switch : 100 Micro Mho

Main Dial : 2.5

Fine balance : 0.08

$$\text{Observed conductance} = \frac{(2.5 + 0.08) \times 100\ \text{K}}{10}$$

$$= 25800\ \text{Micro Mho}$$

Specific conductance (observed conductance multiplied by the cell constant) $= 0.5 \times 25800$

$$= 12900\ \text{Micro mho per cm.}$$

2.8 SILVERING TECHNIQUE

The crystal surface and the optical flats have to be coated with a highly reflecting layer of silver both for microscopic and interferometric studies. The principle of this method is to thermally evapourate. Silver on to the specimen at a very low pressure.

A commercial vacuum coating unit. 'Edwards 12 EA' (fig. 2.21b) was used for this purpose. The vacuum chamber was evacuected by a three stage silicon oil diffusion pump backed by an oil ~~di~~rotary pump. The vacuum at different stages was measured by the piranigauge and Philips ionisation gauge incorporated in the unit. The surfaces were throughly cleaned before deposition of silver. The cleaning process of surfaces dependent very much on the nature of the surfaces. Optical flats were first cleaned with nitric acid, washed with water after applying soap and then with hydrogen peroxide. Thereafter they were cleaned by rubbing with cotton wool till no breath figure was formed on breathing over them. Freshly cleaved crystal surfaces did not require any cleaning. Final cleaning was done by ionic bombardment in vacuum coating unit by means of a high tension discharge.

When the pressure was about 1×10^{-5} torr spectroscopically pure silver was evapourated from a molybdenum boat by passing a low tension high current. In order to protect the surfaces to be coated from receiving the vapours of burnt impurities while heating the boat, it was covered with a adjustable shutter. Silver was deposited for the required time by removing the shutter from above the boat. The specimens were then optically studied.

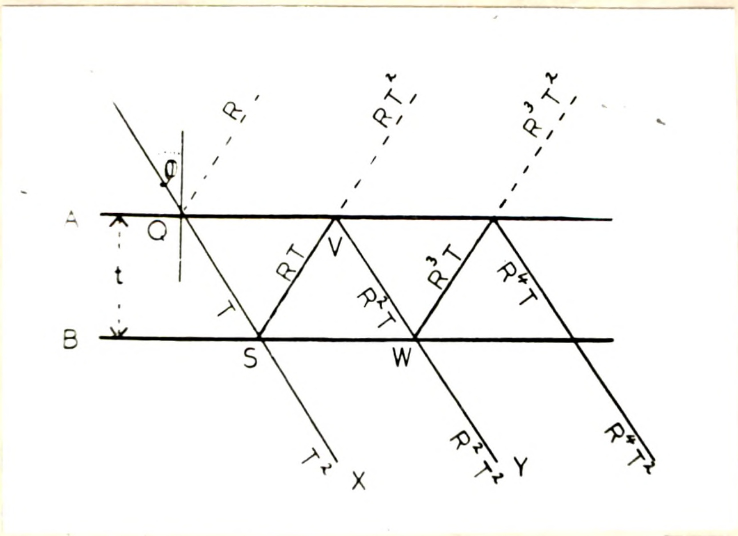

Fig. 2.21a The reflected and transmitted beam intensities in terms of R and T from two component surfaces.

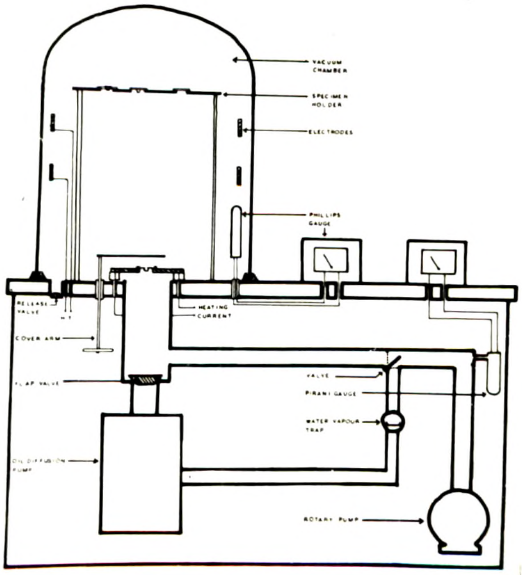

Fig. 2.21b Vacuum coating unit (Edward Co. London).

2.9 INTERFERENCE MICROSCOPY OR MULTIPLE BEAM INTERFEROMETRY

This is a very sensitive technique for the study of crystal surfaces developed by Tolansky.[6] Since the technique is well established, only a few points will be outlined here, having a special bearing on the investigation of crystal surfaces. The two component surfaces (fig. 2.21a) are silvered and having transmission and reflection coefficients T & R respectively. They are parallel and separated by a small distance 't'. They constitute an interferometer. When a monochromatic beam of light is normally incident on the interferometer, the reflected and transmitted beam are as shown in fig. 2.21a. The summation of the transmitted series of multiple reflected beams gives the intensity distribution as

$$I_{max} = \frac{T^2}{(1 - R)^2} \quad \text{at} \quad n\lambda = 2t\cos\theta$$

and

$$I_{min} = \frac{T^2}{(1 + R)^2} \quad \text{at} \quad (n + \tfrac{1}{2})\lambda = 2t\cos\theta$$

If there is no absorption by the component surfaces $R + T = 1$ by definition. The fringe peak maximum without absorption has the same intensity as that of the incident light. Therefore the fringe shape is independent of T and is determined only by the reflectivity R. Even if absorption is taken into account, it can be shown that the absorption merely influences the total intensity and the visibility of fringes. However it does not change the fringe shape.

It should be noted that if the surface to be studied is of opaque specimen it is necessary to observe the fringes in the reflected system. In this case the silvering of the flat is more critical as any absorption in the silver reduces the visibility of the fringes.

The principle factors deciding the usefulness of the multiple beam fringes are the contrast and the sharpness. The contrast may be defined by the term $(I_{max} - I_{min})$ and the sharpness in terms of fringe half width δ which is given by

$$\delta = (1 - R) / \sqrt{2}$$

where R is the geometric mean $\sqrt{R_1 R_2}$, R_1 and R_2 being the reflectivities of the two surfaces. Hence δ is minimum when R is maximum. To achieve a maximum value of R, it is essential to reduce the absorption coefficients as much as possible. The contrast or the visibility of the fringes also depends on absorption especially in the reflected system.

Although Fabry and Perot used a thin wedge silvered on both sides to produce sharp fringes. Tolansky[6] was the first who investigated the critical conditions to be fulfilled for doubly silvered wedges so that a close approximation to the Airy summation can be achieved. He formulated the following conditions :

(1) The surface must be coated with highly reflecting films with minimum absorption.

(2) The film should contour the surface exactly and be highly uniform in thickness.

(3) Monochromatic light or almost a few widely spaced wavelength should be used.

(4) The interfering surfaces should be separated by a few wavelengths of light only.

(5) A parallel beam within 1-3° tolerance should be used.

(6) The incident beam should perfectly be normal.

For rapid measurements a commercial interference microscope (Carl Zeiss Jena) of the type shown in fig. 2.22a was employed. Fig. 2.22b shows the semi silvered optical flat holder (No. 40). The screws No. 41 can be used to tilt the semisilvered flat on surface of specimen by small angle to obtain multiple beam interference fringes or contours.

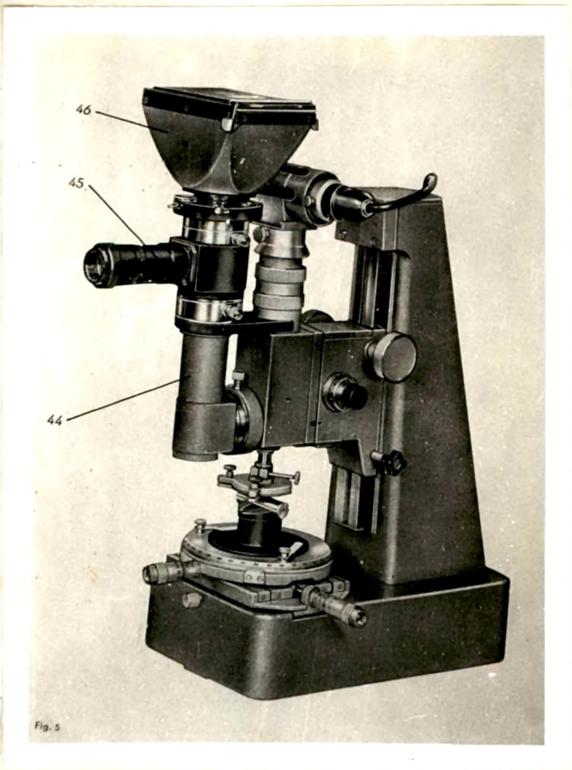

Fig. 2.22a Interference microscope (CZ).

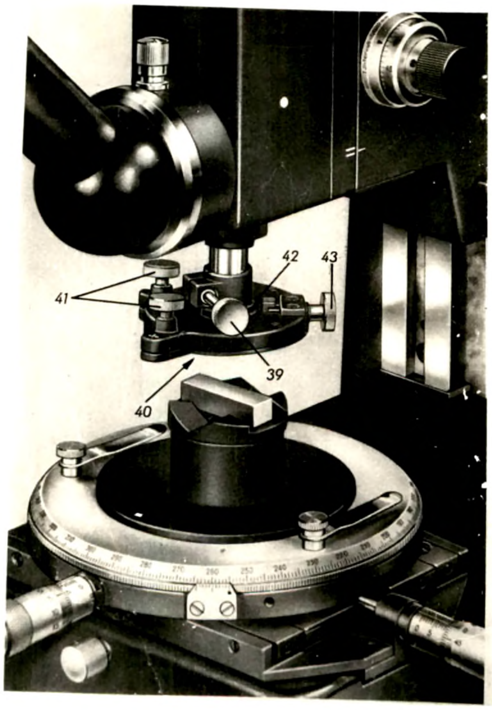

Fig. 2.22b Interference microscope (CZ) showing optical flat holder attached to objective.

2.10 CRYSTAL GROWING TECHNIQUES

2.10.1 Introduction

Basically, the study of solid state physics is nothing but the study of crystals - their structure, defects, properties and growth.

There is a great demand of single crystals of greater and greater purity and perfection in every branch of research connected with the solid state and still greater demand for industrial applications. This has created a considerable interest in the study of growth of single crystals.

2.10.2 Different methods of growing crystals

In recent yeats there are a number of methods which have been developed for growing single crystals of different types of materials. The classification of these methods is as shown below :

(1) Growth from solution

(A) Growth from water solution : (a) By progressively (regularly) varying the temperature (by lowering the temperature) to reduce the solubility and produce crystallization under controlled conditions (e.g. inorganic salts such as alkali halides, Rochelle salt, EDT, ADP etc.)

(b) At constant temperature (i) by progressively decreasing the amount of solvent by evaporating and (ii) by increasing the amount of solute.

(B) Growth from flux (e.g. metals and non-metals, ruby, barite etc.).

(C) Hydrothermal growth (Calcite and zincite etc.).

(D) High pressure growth (boron nitride).

(E) Growth by gel method.

(F) Growth by electrodeposition.

(2) Growth from melt

- a. Bridgman-Stockbarger method.
- b. Zone melting method.
- c. Verneuil flame fusion method.
- d. Czocharlski - Kyropoulos method.

(3) Growth from vapour(Gas) phase

(Silicon carbide, cadmium sulphide, lead sulphide, zinc telluride, lead telluride etc.).

(4) By chemical decomposition

(Koref hot-wire method)

(5) By strain anneal method.

(6) From high temperature solution

(Growth of mica, tourmaline).

(7) From low temperature solution

A survey of methods of growth suggest that almost 80% of crystals grown are from the melt method. There are several standard books available on the growth of crystal by different methods (Buckley[8], Gilman,[1] Lawson & Nelson[9] etc.).

'Growth from melt' has been found to be most successful method for growing large single crystals of semi conducting materials and alkali halide materials. All the methods of growth from a melt rely on cooling the liquid below its freezing point.

The basic condition to be satisfied for the production of single crystals from melt is that a progressive freezing of the liquid takes place in a controlled manner. In other words the solid-liquid interface moves in a controlled manner along the growth axis. The growth rate of the crystal is the rate at which this solid-liquid interface moves in a direction perpendicular to the interface.

Generally the growth of single crystal from melt is influenced by the rate of growth, the temperature gradient along the solid and impurities. There are several factors which limit the application of this method:

(i) The method is applicable only when the substance melts congruently and without irreversible decomposition. (ii) There should not be solid state phase transformation between the melting point and, the temperature to which the crystal will later be cooled. (iii) The temperatures required in growing crystals directly from pure melt are usually higher than those required by other methods. For this purpose, the furnace design and temperature control are important. The selection of a suitable material for crucible or container of the molten substance at elevated temperatures without contamination is also important.

The present author used the modified kyropoulos method to grow single crystals of sodium nitrate from melt. Single crystals of sodium nitrate were also grown from solution by controlled slow cooling method.

2.10.3 Kyropoulos method

This method was developed by Czocharalski[10] in 1918 although it is sometimes named after kyropoulos[11] who worked on the technique in 1926. It is crystal-pulling technique describing the slow pulling of the crystal from melt. Essentially a small single crystal seed is dipped into the surface of the melt and slowly withdrawn at the rate at which the crystal solidifies, while remaining in contact with the melt. If suitable precautions (e.g. avoidance of thermal and mechanical fluctuations) are taken the material withdrawn from the melt solidifies as a large single crystal. This method is slightly modified by employing rotation mechanism of seed to avoid radial temperature gradient and impurities. The water cooling system for seed is also employed to keep the temperature of seed slightly lower than melt.

Difficulties were experienced by a number of workers (e.g. Stober[12], West[13], Yamaguti[14]) to grow large single crystals of sodium nitrate. Using modified Kyropoulos method large single crystals of $NaNO_3$ were grown (Komnik and Startsev[15]). This method was followed by the author to grow these crystals in the laboratory. There are certain specific properties of sodium nitrate crystals which are required to be considered for obtaining good quality crystals.

They have pronounced thermal conductivity anisotropy, the thermal conductivity being maximum in the direction of optic axis viz. $[111]$. The maximum rate of growth proceeds in this direction. As a result, if the direction of the growth does not coincide with the $[111]$ direction, the crystal grows in blocks. The anisotropy of the heat expansion coefficient leads to thermal stresses on cooling the single crystals. The effect is enhanced by the anamalous change of thermal expansion near 275°C, where the phase transition of the second type takes place (M. Kantola and E. Vilhonen[16] ; A Mustajoki[17]). Hence the following requirements should be provided for obtaining crystals free from stresses.

(1) The growth must coincide with the [111] direction,

(2) The crystal must grow without any container and

(3) The cooling after annealing must be slow.

In the present case the axis of the growth of single crystals of $NaNO_3$ on insoluble mica disc employed as a seed coincided with [111] direction. The pulling of the seed was carried out in the usual manner. The schematic diagram (fig. 2.23a) indicates in detail the method of growth of $NaNO_3$ crystal. The photograph (fig. 2.23b) shows the crystal pulling unit with furnace, temperature controller, power supply, rotation mechanism etc. The crucible furnace of 80 mm in diameter and 200 mm in depth with side (1) and bottom (2) heaters was used. The bottom heater has a constant stabilized voltage supply. The power of the side heater is adjusted by the potentiometer. The thermocouple (3) placed near the coil of the side heater serves as a pickup. The furnace has a cover (4) with two windows provided for observation of crystal during its growth. In the centre of the cover there is an opening for

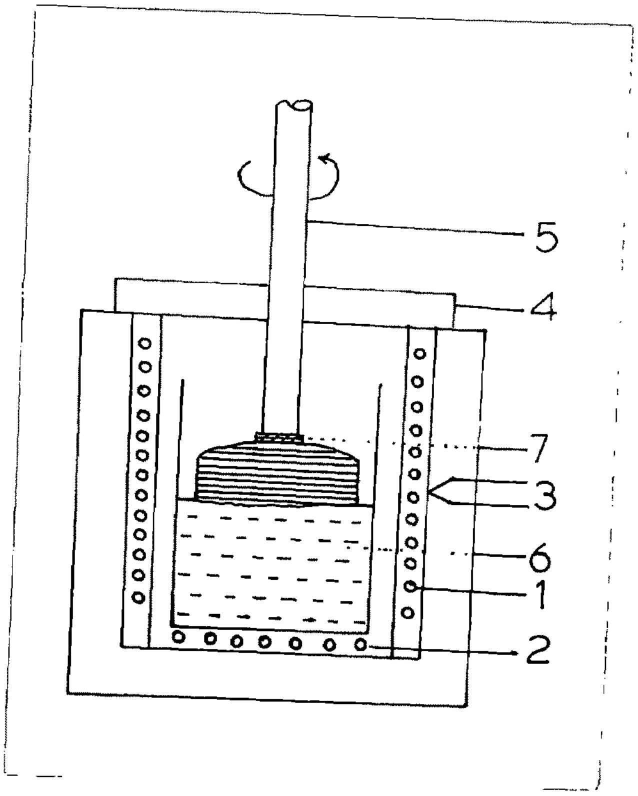

Fig. 2.23a Schematic diagram of method of growth of sodium nitrate crystals from melt.

1. Side heater
2. Bottom heater
3. Thermocouple
4. Mica window
5. Cooler
6. Crucible
7. Mica seed

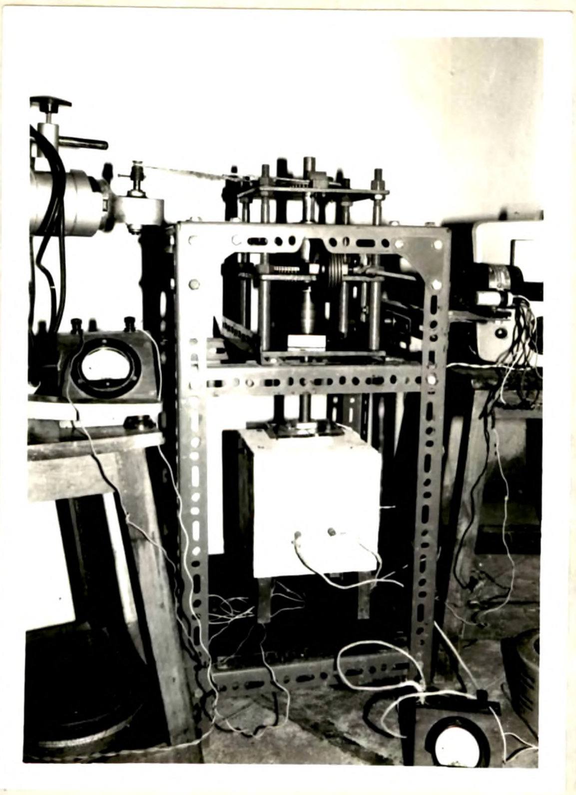

Fig. 2.23b Crystal pulling unit along with furnace, temperature controller, power supply, rotation mechanism etc.

the cooler (5), a rotating copper rod of 20 mm in diameter acts as the cooler (the water cooling is not required). The crystals are grown in aluminium crucible (6) of 70 mm in diameter, 80 mm height and 0.8 mm of wall thickness. As a seed muscovite mica disc (7) of 21 mm in diameter and 0.5 mm thickness was used. It was glued to the edge of the cooler by BF-2 agent. The crystals were grown from the raw material of G.R. quality supplied by Sara Merk, India (the contents of the assay are given in a tabular form Table 2.2).

Both heaters were switched on and when the temperature of the crucible containing powder of sodium nitrate crossed the melting point (308°C) the charge was in molten condition. The temperature of the melt was not allowed to exceed 340°C, as $NaNO_3$ decomposes at 380°C. The cooler with the seed glued on it was initially kept 2 mm away from molten surface. It was gently immersed in the heated melt so that mica came in contact with the liquid-surface. The seed was kept in this position for 30 min. Then the cooler was slowly lifted so as to maintain contact between mica and melt and almost at the same time it was rotated at rate of 2 rpm and the temperature was lowered at the rate of 2 degrees per hour by potentiometer using only side heater. The power fed to the bottom heater was kept constant. The cooler was raised at a rate of 2 mm

Table 2.2

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GUARANTEE CERTIFICATE

Sodium nitrate ($NaNO_3$) for analysis Guaranteed Reagent
Mol. wt. 84.99

Insoluble portion	Maximum
Free acid (as HNO_3)	0.003 %
Free alkali (as NaOH)	0.003 %
Ammonium salts (NH_4)	0.002%
Arsenic (As)	0.0004%
Calcium (Ca)	0.002 %
Total chlorine content (Cl, ClO_3, ClO_4, as Cl)	0.004 %
Chloride (Cl)	0.0005%
Heavy metal (as Pb)	0.0005%
Iron (Fe)	0.0003%
Iodate (IO_3)	0.000025%
Magnesium (Mg)	0.0005%
Nitrite (NO_2)	0.00005%
Phosphate (PO_4)	0.00025%
Potassium (K)	0.005 %
Sulphate (SO_4)	0.003 %
Assay ...... (mini)	99.5 %

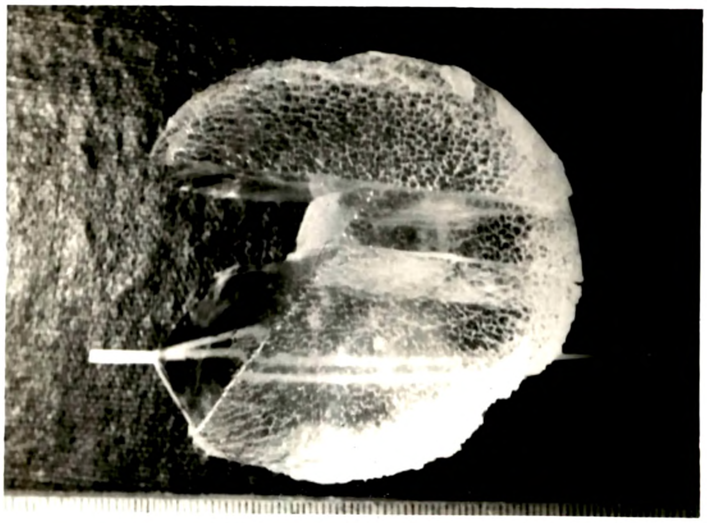

Fig. 2.24 Sodium nitrate crystal grown from melt exhibits double refraction of a strip placed below the crystal.

per hour. Thus single crystals of 15 to 20 mm height and about 60 mm in diameter could be grown in 10 hours. The grown crystal was transported with heated spincer into another furnace for annealing, where it was kept for four hours at 270°C and then the temperature of the furnace was lowered at a rate of 3 degrees per hour. The crystals thus obtained were transparent and exhibited characteristic properties such as perfact cleavage, double refraction etc. (fig. 2.24).

2.10.4 Crystal growth from solution

Single crystals of sodium nitrate were also grown from solution, by following simple method (Holden and Singer[18]).

The solubility of $NaNO_3$ per 100 cc. of distilled water at different temperatures is given below :

Quantity of $NaNO_3$ in gms. per 100 c.c. of water	73	80	88	98	104	113	122	133
Temperature °C	0	10	20	30	40	50	60	70

The graph of quantity of $NaNO_3$ in gms. per 100 c.c. of water Vs. temperater in °C is shown in figure 2.25.

Using above data a just saturated solution of sodium nitrate (GRSM quality) was made by dissolving it in doubly

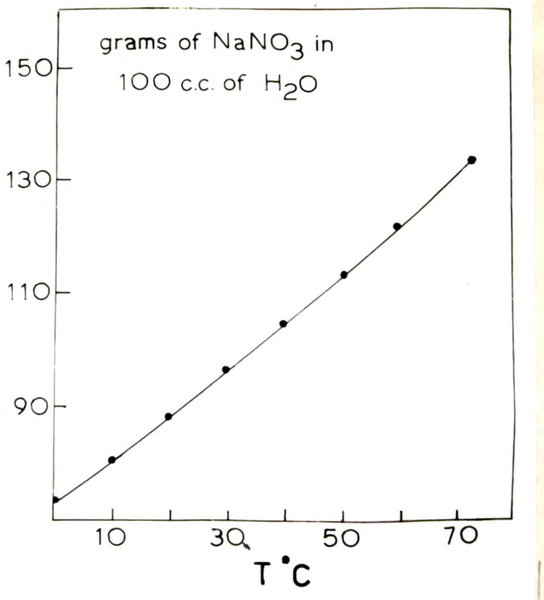

Fig. 2.25 Graph of solubility of sodium nitrate vs temperature.

Fig. 2.26 Growth of sodium nitrate crystals from solution in sealed bottles.

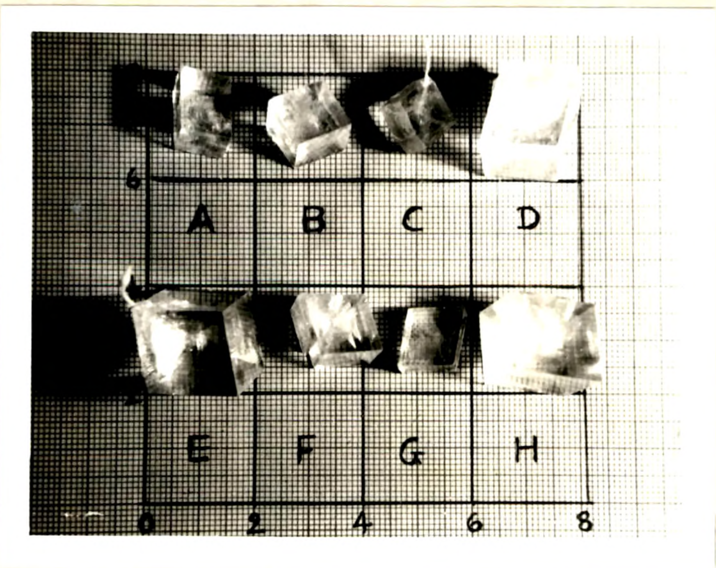

Fig. 2.27 Sodium nitrate crystals grown from solution.

distilled water. This filtered solution kept in to a few petry dishes was evaporated at constant temperature to obtain good transparent seeds of 4 to 5 mm size.

A saturated solution was made in the usual manner at 40°C by dissolving 104 gms. of $NaNO_3$ powder per 100 c.c. of doubly distilled water. This solution was filtered and filled in a bottle. The seed crystal properly tied was suspended in this bottle. Several bottles with proper seeding and lids were placed in an incubator to have control of temperature for crystal growth. With slow cooling at the rate of 0.5°C per day fairly large transparent well developed rhombohedral crystals could be grown in a fortnight (fig. 2.26). A few crystals were milky and had some veils. They were discarded (fig. 2.27). It was observed from study of electrical conductivity of melt grown and solution grown crystals of $NaNO_3$, that the solution grown crystals were of inferior quality (Bhagat[19]).

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CHAPTER - III

ANALYSIS OF STRAIGHT LINE PLOTS

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ANALYSIS OF STRAIGHT LINE PLOTS

PAGE

3.1 INTRODUCTION

No physical measurement is absolutely correct. It is always associated with an error. The final result in an experimental 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] 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]

In the present work relations between hardness on cleavages of synthetic single crystals of $NaNO_3$, 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 or between dissolution rate and temperature of dissolution or between dissolution rate and etchant concentration for studying dissolution phenomena on cleavage surfaces under controlled conditions of chemical or thermal etching 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 are 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 :

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

(2) Estimation of $y = mx + c$ by the method of zero sum,

(3) Centroid method to estimate $y = mx + C$.

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

(5) Statistical estimation of best straight line.

3.2 VISUAL ESTIMATION OF THE BEST STRAIGHT LINE

Graphs of log p Vs log d (Cf. Chapter V), of $\log \bar{H} T_Q$ Vs $\log T_Q$ (Cf. Chapter VI and Appendix) and $\log \sigma_c T^{1-k}/\bar{H}$ Vs $1/T$ (Cf. Chapter VI) were plotted in the usual way taking adequate care to choose the scales so that the points were not crowded together over a small range. The best straight line through the plotted data was determined by using taut black thread or a solder wire or a transparent ruler. The accuracy of the method is influenced by extreme observations.

Cases arise in practice where two extreme straight lines can be drawn to represent the observations. The difference in gradient between these two lines will give some measure of the error in the slope and of the intercept. The mean slope is usually taken. This procedure is usually applicable where exact relations between the plotted quantities are theoretically or empirically known.

The possibility exists that only four observations (Two pairs of extreme observations) will control the conclusions from an experiment. This may be acceptable in cases where the quality of the work is precise and the errors are small. Where there is considerable spread in the observations, the temptation exists to ignore observations thought to be 'too far out', thereby introducing a personal judgement which may turn out to be an error in the final objective analysis. In the present case the percentwise spread in observations in general from the mean and also for a pair of extreme observations and percentage change in the slopes and intercepts for the pairs of extreme observations were calculated to show that the present method followed by the author, graphically treats the concerned observations fairly accurately.

3.3 ZERO SUM METHOD TO ESTIMATE THE BEST STRAIGHT LINE

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

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

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

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

solving the above two simultaneous equations,

$$m = \frac{Y_1 - Y_2}{X_1 - X_2}, \qquad \ldots\ldots(3.3)$$

$$C = \frac{(Y_1 + Y_2) - m(X_1 + X_2)}{n} \qquad \ldots\ldots(3.3)a$$

$$\therefore C = \frac{(Y_1 + Y_2)(X_1 - X_2) - (Y_1 - Y_2)(X_1 + X_2)}{n(X_1 - X_2)} \qquad \ldots\ldots(3.4)$$

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.

3.4 CENTROID METHOD FOR OBTAINING THE BEST STRAIGHT LINE

This method was developed by Cauchy and also independently by Aubery. It is useful when the number of pairs of observations exceeds 6 and that the independent variable x is known accurately and equally spaced.

(a) Suppose there are n pairs of observations :

$$(x_1\ y_1)$$
$$(x_2\ y_2)$$
$$(x_3\ y_3)$$
$$(x_n\ y_n) \qquad \ldots. \ (3.6)$$

and the relation between them is linear. A point (X, Y) is called the centroid of all the points and is calculated

$$X_1 = \sum_{r=1}^{i} x_r/i$$
$$Y_1 = \sum_{r=1}^{i} y_r/i \qquad \ldots. \ (3.7)$$

and also for (n - i) values as

$$X_2 = \sum_{r=i}^{n} x_r/(n - i) \; ; \; Y_2 = \sum_{r=i}^{n} y_r/ n - i \qquad \text{....(3.8)}$$

The best value of the slope of the straight line joining (X_1, Y_1) and (X_2, Y_2) is

$$m = \frac{Y_2 - Y_1}{X_2 - X_1} \qquad \text{....(3.9)}$$

and the intercept

$$C = Y - mX \qquad \text{....(3.10)}$$

(b) Another variation of the above method is sometimes used. Divide the pairs of observations into three (al_most) equal parts obtain the centroid for each part, namely lower (ℓ), central (C) and upper (u) and also for n points

$$X_\ell = \sum_{r=1}^{n/3} x_r/n/3 \; ; \; Y_\ell = \sum_{r=1}^{n/3} y_r\Big/n/3 \qquad \text{....(3.11)}$$

$$X_c = \sum_{r=n/3}^{2n/3} x_r\Big/n/3 \; ; \; Y_c = \sum_{r=n/3}^{2n/3} y_r\Big/n/3 \qquad \text{....(3.12)}$$

$$X_u = \sum_{r = 2n/3}^{n} x_r \Big/ n/3 \quad ; \quad Y_u = \sum_{r = 2m/3}^{n} y_r \Big/ n/3$$

....(3.13)

$$\overline{X} = \sum_{r = 1}^{n} x_r \Big/ n \quad ; \quad \overline{Y} = \sum_{r = 1}^{n} y_r \Big/ n$$

....(3.14)

Then draw the best straight line through the points (x_c, y_c), (X_ℓ, Y_ℓ), $(\overline{X}, \overline{Y})$ and (X_u, Y_u) so that three points are on the line or are evently scattered, n pairs of observations are also plotted on the same graph. The slope m and intercept C are found in the usual way.

The distinct advantages of this method are as follows :

(i) It permits an estimate to be made of the standard error of the slope m.

(ii) Agreement is good with the statistical least squares calculation (cf. method V Art 3.1).

For determining the standard error of the gradient, the range ω defined by the distance (p) in the y direction from the best line of the point farthest above the line and the distance (q) of the point farthest below the regression line is found. Note that the points mentioned above may be any one from the (n + 3) pairs of observations plotted in the graph. The standard error of the slope is given by

$$\frac{4W}{n\ (x_n - x_1)} \qquad \ldots\ (3.15)$$

where $W = p + q$ .... (3.16)

and the standard deviation of $\overline{Y}$ is W / n.

If the best straight line does not pass through the origin, the intercepts are x_o and y_o given by

$$x_o = \overline{X} - \overline{Y}/m \qquad \ldots\ (3.17)$$

$$y_o = \overline{Y} - m\overline{X} \qquad \ldots\ (3.18)$$

The errors of x_o and y_o are found by the usual error propagation formula.

3.5 ESTIMATION OF $y = mx + C$ FROM DATA USED IN A SPECIFIC MANNER

Values of independent variable x are taken at n equally spaced intervals and the equations multiplied by 1, 2, 3, ... n, the n original equations and the newly obtained n equations are summed to obtain two equations.

These two equations are solved to obtain slope (m) and intercept C. Suppose there are n pairs of observations arranged in such a manner that x values are equally spaced in an ascending order.

x	Original equation $y = mx + C$		New equation
1	$y_1 = m + C$	multiplied by 1	$y_1 = m + C$
2	$y_2 = 2m + C$	multiplied by 2	$2y_2 = 4m + 2C$
3	$y_3 = 3m + C$	multiplied by 3	$3y_3 = 9m + 3C$
4	$y_4 = 4m + C$	multiplied by 4	$4y_4 = 16m + 4C$
.			
.			
n	$y_n = nm + C$	multiplied by n	$ny_n = n^2m + nC$

$$\sum_{r=1}^{n} yr = \sum_{r=1}^{n} rm + nC = m \sum_{r=1}^{n} r + nC \quad \text{....(3.19)}$$

$$m = \frac{n \sum ry_r - \sum y_r \cdot \sum r}{n \sum r^2 - (\sum r)^2} \quad \text{....(3.20)}$$

$$C = \frac{\sum y_r - m \sum r}{n} = \frac{\sum y_r}{n} - \frac{m \sum r}{n}$$

$$\text{.....(3.21)}$$

where,

$$\sum_{r=1}^{m} ry_r = \sum_{r=1}^{n} r^2 m + \sum_{r=1}^{n} rc$$

$$= m \sum_{r=1}^{n} r^2 + c \sum_{r=1}^{n} r$$

$$= m \sum r^2 + \sum r \; \frac{\sum y_r - m \sum r}{n}$$

$$\therefore \; n \sum ry_r = m\,n \sum r^2 + \sum r \cdot \sum y_r - m \left(\sum r\right)^2$$

$$\therefore \; n \sum r\,y_r - \sum y_r \cdot \sum r = m \left\{ n \sum r^2 - \left(\sum r\right)^2 \right\}$$

3.6 STATISTICAL ESTIMATION OF BEST STRAIGHT LINE

There are two ways of estimating statistically the best straight line : (a) Regression of y on x and (b) Regression of x on y. In both these methods one variable is 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.

$$\text{Let} \quad Y_1 = mx + C \qquad \text{.... (3.22)}$$

where Y_1 is not the observed value y_1 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

$$y_1 - Y_1 \quad \text{for} \quad y = y_1 \qquad \text{.... (3.23)}$$

Assuming an equation of the form

$$y = mx + C.$$

for which values of m and C are required such that,

$$(y - Y)^2 = E \qquad \text{.... (3.24)}$$

is a minimum.

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

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

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

$$\text{.... (3.25)}$$

For E to be minimum

$$\frac{dE}{dm} = 0, \qquad \frac{dE}{dC} = 0$$

Differentiating E w.r.t. m yields

$$\frac{dE}{dm} = \sum_{1}^{n} (-2yx + 2mx^2 + 2x\,C) = 0$$

$$= \sum_{1}^{n} 2(mx^2 + xc - xy) = 0$$

$$\therefore \sum_{1}^{n} xy = m \sum_{1}^{n} x^2 + c \sum_{1}^{n} x \qquad \ldots (3.26)$$

Now differentiating 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

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

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

$$= nc + m \sum_{1}^{n} x \qquad \ldots (3.27)$$

Solving the equations for C

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

$$\therefore \quad C = \bar{y} - m\bar{x} \qquad \ldots. \ (3.28)$$

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

$(\bar{x}, \bar{y})$ represent the mean of all coordinates x and y. The best straight line passes through the mean of all coordinates. Substituting value of C from (3.28) in equation (3.26) gives,

$$\begin{aligned}
\sum xy &= m\sum x^2 + (\bar{y} - m\bar{x}) \sum x \\
&= m\sum x^2 + \bar{y}\sum x - m\bar{x}\sum x \\
&= m\sum x^2 + \frac{\sum y}{n}\sum x - m\frac{\sum x}{n} \cdot \sum x \\
&= m\sum x^2 + \frac{\sum y \sum x}{n} - \frac{m}{n}(\sum x)^2
\end{aligned}$$

$$\therefore \quad \sum xy - \frac{\sum x \cdot \sum y}{n} = m\left[\sum x^2 - \frac{(\sum x)^2}{n}\right]$$

$$\therefore \quad m = \frac{\sum xy - \frac{\sum x \cdot \sum y}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

$$= \frac{\sum (x - \bar{x}) \quad (y - \bar{y})}{\sum (x - \bar{x})^2} \qquad \ldots\ldots (3.30)$$

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

$$y = mx + C \qquad \ldots\ldots (3.31)$$

where m is called the regressing 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 coordinates are

$$\bar{X} = \frac{\sum x}{n} \qquad \ldots\ldots (3.32)$$

$$\bar{Y} = \frac{\sum y}{n} \qquad \ldots\ldots (3.33)$$

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

$$C = \bar{x} - m\bar{y} \qquad \ldots\ldots (3.34)$$

and $$m = \frac{\sum(x - \bar{x})\ (y - \bar{y})}{\sum(y - \bar{y})^2} \qquad \ldots.(3.35)$$

and the best straight line is

$$x = my + C \qquad \ldots.(3.36)$$

where C and m are given by equations..(3.34) and (3.35).

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