PART I

GENERAL INFORMATION ON CALCITE, POTASSIUM CHLORIDE AND EXPERIMENTAL TECHNIQUES

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PAGE

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1.1 GENERAL INFORMATION ON CALCITE:

1.1.1 INTRODUCTION:

In the entire mineral kingdom, next to quartz 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 mineralogy. 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 (1952), Dana and Ford (1951) and Rogers (1937) have given a nice account of calcium carbonate (calcite).

1.1.2 OCCURRENCE:

It occurs in nature in several localities and ranges in character from pure transperent single crystals to large conglomerate masses which are quite opaque. It occurs; (1) in veins, cavities and amygdules, due to penetration of calcareous solutions, (2) as a cellular tissue of many phanerogamia, e.g. cycadeae and cactaceae, (3) as a rock forming minerals in the sedimentary cycles and in great thickness in relatively pure form as chalks and limestones, (4) as a biogenic mineral forming limestones, organisms such as mollyseas, branchiopads, corals and crinoids contributing their shells or other hard parts, (5) as a diverse from, calcareous sinter or tufa or travertine; the tophus of pling and the lapis fiburatinus of pling and vitruvius and formation of stalactites and stalagmites in caves, (6) as a paramorph after argonite, calcite is the stable form of calcium carbonate under ordinary conditions.

1.1.3 CRYSTAL COMPOSITION:

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. These 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 accompanying variation in composition are not fully established, especially in the polycomponent system.

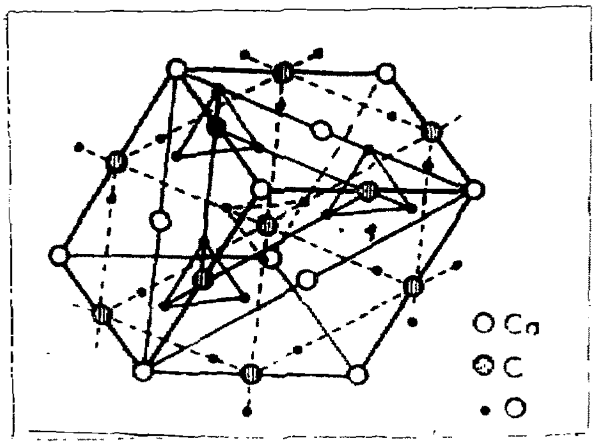

FIG. 1·1

1.1.4 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 rhombohedral 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 in 1914. He later on derived (1924) the optical properties of both calcite and its polymorph aragonite in terms of the atomic structure. In the fig. 1.1, calcium atoms are represented by blank 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, consisting of central carbon atoms surrounded by an equilateral triangle of oxygen atoms in a plane at right angles to diagonal (i.e. the plane of the paper). On account of the space occupied by these 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°.

1.1.5 FORM AND HABIT:

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

Crystals show four distinct habits (1) rhombohedral, (2) prismatic, (3) scalenohedral and (4) 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 the so-called dog-tooth spar, nail-head spar and satin spar. It is a fibrous variety with a silky lustre resembling the satin spar 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 contains manganese carbonate and is known as mangano-calcite, ferro-calcite containing ferrous carbonate and calcite etc.

1.1.6 CLEAVAGE, GLIDING AND TWINNING:

It has a perfect rhombohedral cleavage, a cleavage in three directions at oblique angles (74°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 (Tolansky and Khamsavi, 1946). The cleavage spacing between rhombohedral faces is 6.1 A°. The crystals cleave so readily that light blows will shatter them into fragments and as they are soft enough to be readily scratched with a knife, extreme care has to be excercised in handling them. There is often parting parallel to $\{01\bar{1}2\}$ and this is sometimes better developed than the cleavage itself. Some specimens of calcite show parting parallel to $\{0001\}$. Fracture is conchoidal but difficult to produce, since it is brittle.

Four twinning laws are known for calcite (1) 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. (2) 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. (3) 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. (4) Twin plane $\{02\bar{2}1\}$ is rare with composition plane $\{02\bar{2}1\}$.

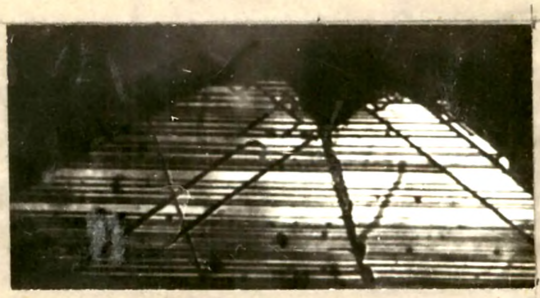

FIG.1·2

1.1.7 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 crystals, two cleavages making an obtuse angle (102°) with each other developed and extended outwards from the edges of that area (fig. 1.2). 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 of contact and only on one side of it. These lines are equally inclined to the two sets of cleavages and may be explained as being due to glides occurring within the crystal along the direction of a rhombohedral edge (Raman, 1959).

Percussion mark can be also be observed by a sharp quick blow with a dull conical point on a calcite cleavage surface. The percussion mark is much helpful in determining the orientation of the crystal. The whole percussion figure with the point of impact as the vertex of the triangle formed by the two cleavages and the series of lines is orientated oppositely 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 boundaries are determined.

1.1.8 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 μ_o = 1.658 and μ_e = 1.486 (Bragg, 1924). 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 (Smartt and Steel, 1959).

Hardness on Moh'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 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 recognized by their easy solubility with brisk effervescence in cold diluted acids, the properties possessed by no other common minerals resembling calcite.

1.1.9 USES:

Finest variety of calcite, known as iceland spar is used in optical apparatus especially for the polarizing 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 multifarious uses is given by Searle (1935) and a physico-chemical survey of high grade Indian limestones is done by Bijawat and Sastri (1957). 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. At the time of second world war, calcite was replaced by sodium nitrate in polarizing microscope, due to shortage of calcite. Since sodium nitrate is hygroscopic, precautions are taken to keep it free from moisture. However it could not completely replace the calcite crystals.

1.2 GENERAL INFORMATION ON POTASSIUM CHLORIDE:

1.2.1 INTRODUCTION:

Potassium chloride which was called sylvius salt, is the main product of the action of muratic acid on the ashes of land plants. Excellent account on natural crystals of potassium chloride known as sylvite is available in many standard books on mineralogy (e.g. see Rogers, 1937; Dana and Ford, 1957 etc.).

1.2.2 CRYSTAL COMPOSITION:

Potassium chloride has a formula KCl (K = 52.44% and Cl = 47.56%). The natural crystals are often associated with halite but do not contain NaCl in solid solution as one might expect.

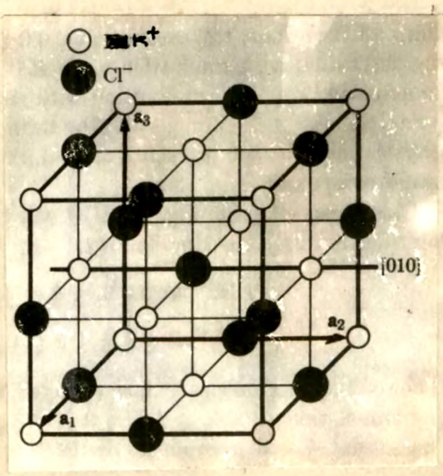

FIG 1·3

1.2.3 GROUP AND STRUCTURE:

Potassium chloride belongs to the isometric system, hexoctahedral class ($4/m\ \bar{3}\ 2/m$) with space group Fm3m.

The crystal structure of potassium chloride studied (Bragg, 1914) by X-rays, indicates that the arrangement of the atoms is that of a face centred cubic lattice (fig. 1.3), with plagihedral cubic symmetry because of marked different in size of atoms. The atoms are apart in space lattice by 3.141×10^{-8} cm, and the lattice energy is 159.0 cals/mol.

The results obtained by etching the crystal (KCl and NaCl) at ordinary temperatures indicate that the intra-molecular forces of a potassium chloride crystal differ from those of the sodium chloride crystal or more precisely, that the certain lattice regions are more closely united in the potassium chloride, whereas the same is not the case in sodium chloride.

1.2.4 FORM AND HABIT:

The natural crystals of potassium chloride occur in cleavable and granular masses and in well formed cubic or less commonly cubo-octahedral or octahedral crystals.

1.2.5 CLEAVAGE, GLIDING AND TWINNING:

It has perfect cleavage {001} . The crystals are soft enough to be readily scratched with a knife, Hence extreme care has to be exercised in handling them. Fracture is uneven. If small pieces in the form of cubes are pressed between glasses along cleavage directions, potassium chloride flattens like a piece of wax but sodium chloride breaks to a powder because potassium chloride is not as brittle as sodium chloride. Potassium chloride scratched normal to a cube edge does not show barbed isosceles triangles that sodium chloride does. Further translation gliding with T {011} , t [011] and also with T {001} , t [011] is reported. Twinning on {111} , is observed only in artificial crystals.

1.2.6 PROPERTIES:

For pure natural crystals specific gravity is 1.993 ± 0.005. It is usually colourless and transparent or white when pure. The colour varies from white to dirty gray, bluish, yellowishred to red, the red tints are usually due to included particles of hematite. Taste is much like that of sodium chloride, but somewhat bitter. It is highly diathermous.

In transmitted light it is isotropic along ⟨100⟩ ($n = 1.490$, $n <$ clove oil). Weak anomalous birefringence is sometimes observed, especially in mechanically deformed crystals, and in coloured crystals this effect may be accompanied by distinct pleochroism. Under microscope, fragments are found to have square or rectangular outlines, have moderate relief in clove oil, and are dark between crossed nicols. It is easily fusible, colouring the flame violet. With CuO in a $NaPO_3$ bead it gives an azure-blue flame.

It is soluble in water (34.7 gm in 100 cc of water at 20°C). Its M.P. = 790°C, and B.P. = 1500°C under atmospheric pressure. Its hardness on Moh's scale is 2; it is varying somewhat on different planes and in different directions.

1.2.7 USES:

Used as a fertilizer, as a source of potassium salts and Laser windows.

CHAPTER II

EXPERIMENTAL TECHNIQUES

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2.1 INTRODUCTION:

The various experimental techniques employed during the 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. Silvering technique is used for obtaining better resolution and contrast of the microstructures on crystal surfaces. To study the plastic deformation and other related phenomena the static indentation technique is employed. The diamond pyramidal indenter is used with Vickers Projection Microscope.

Fig. 1

VICKERS PROJECTION MICROSCOPE

set up for the micro examination of a metallurgical specimen.

FIG. 2·1

Further other techniques such as Kyropoulos method, for growing potassium chloride crystals, etch method, conductivity method are also described in this chapter. The techniques mentioned above are well discussed in several standard text books (Buckley, 1952; VanBueren, 1960). Hence only a brief description together with their salient features will be given here.

2.2 VICKERS PROJECTION MICROSCOPE (V.P.M.):

The microtopographical and related studies of crystals were made with the help of Vickers Projection Microscope (inverted metallurgical type) (Fig. 2.1). The specimen to be observed is kept on a freely movable stage above the objective and both the transmission and reflecting systems can be used by simply moving the collimating system, up or down. This microscope consists of a universal illuminator housing, a semi-reflecting plate, iris lens and the objective lenses. The collimating system comprises of powerful mercury or point-o-lite lamp, a condenser and an aperture controlled by an iris diaphragm. Translational movement in two mutually perpendicular directions of the lamp permits centering of the diaphragm. An image of the source can be formed on the field iris.

Movement of the lamp and condenser perpendicular to the axis of the microscope, makes it possible to vary the convergence of light incident on the specimen.

For visual observations, an eyepiece with a reflector is pushed below the objective. For photomicrography, a projection eyepiece is used and the final image is formed after reflection in the projection mirror, in the plane of the screen. Very slight refocussing is necessary when the visual system is changed over to the projection system.

It should be noted that spherical aberration for high power objectives or lenses should be zero for clear image. Different kinds of lenses such as achromatic, fluorite and apochromatic were used to minimize different types of aberration for different wavelengths.

The resolving power is, in the final analysis, the fundamental quality which imposes a practical upper limit on the magnifying power of the microscope. The maximum useful magnification of light microscope is about X2500, It is possible to enhance the magnification beyond this value, but very little is gained by doing so, due to the limit in resolving power imposed by the wavelengths of the light employed. The resolving power of a lens is given by $h = \frac{\lambda}{2N \sin u}$ where λ is the wavelength of light employed. It is clear from this formula that there are three ways to decrease the least resolvable separation h, (i) by decreasing (ii) by increasing angle u in the object space (iii) by increasing the refractive index N in the object space. i.e. by using oil as an immersion fluid, which should be non-drying. The distance between objective lens and specimen at the time of focus is known as working distance, 'h' is much less when oil is used to increase resolution. Specimens observed in the above method are usually spoiled due to oily contamination of the surface. Like resolving power, depth of focus is largely dependent on the objective design. The depth of focus is approximately inversely proportional to the square of N.A.

V.P.M. used in the present study, has advantages and disadvantages over many other microscopes. The microscope, as such is easy to handle and has no restricted working conditions. A large number of accessories can be easily fitted with V.P.M., e.g. polarizing equipment, microhardness tester, phase contrast equipment, light profile adjustment, accessories for observing Fizeau and Feco fringes. All these help in carrying out the study over a large varied field with equal ease and high sensitivity. In addition, both transmission and reflecting systems can be utilized for transparent and opaque crystals without difficulty. Macro- and micro examination of the specimens can be carried out with ease.

Of course, the magnification and resolution obtained with an electron or field-ion-microscope is quite high, but this is only the lateral magnification. It does not give adequate normal resolution. The Vickers microscope with its light profile equipment or with the multiple beam interference technique, can be used to determine heights and depths of various features on crystal surfaces. The order of accuracy by light profile is 0.1 micron, while with the interference method it is about $\lambda/2$ and under favourable conditions it can determine heights and depths of a few angstrom units. Depending upon the nature of the surface features, observed in the present work a judicious choice of objective, eyepiece and bellow distance was made for obtaining desired magnification and resolution.

2.3 LIGHT PROFILE MICROSCOPY:

The light profile technique of Tolansky (1952) is an improvement of Schmaltz's (1936) "light cut method". Here a parallel line graticule is fitted into the housing of field iris of the V.P.M. The images of the lines are formed on the surface of the specimen. However, if the metal tongue internal reflector which is a metallized sector of about 30° angle is used, it sends an off-centred beam of rays which is incident on the specimen at an angle of about 30°. When high power lens is used and when some irregularities are present on the specimen surface the images of the slit will no longer be straight, they will show some shift. This shift can be measured by a filar micrometer eyepiece fitted in the visual eyepiece tube. From the shift in the profile, the actual depth or height of the surface features can be easily calculated, if the values of the constants for different objectives used with the microscope are known. This constant is due to difference in magnification of profile and linear magnification of microscope. The constant quantity for a particular objective should be multiplied by linear magnification for obtaining magnification of profile. The values of the constant for different objectives used with the microscope in this work are as follows:

	Oil immersion	Dry objective	
Objective	1.8 mm	4 mm	8 mm
Constant	1	1.38	0.56

The present "light profile technique" has following advantages over the original "Schmaltz's light cut method".

(1) The magnification was restricted to 400 diameters for light cut method, while in light profile it was up to 2000 diameters.

(2) In light cut method, the surface having the irregularities was not visible, while in light profile it is clearly observed, Hence interpretation of the results becomes easier.

(3) For light cut technique, a special apparatus is required to be prepared with two microscopes at

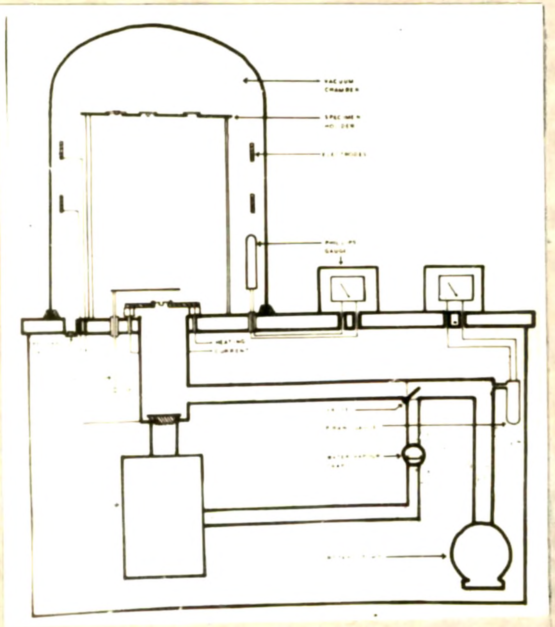
VACUUM CHAMBER
SPECIMEN HOLDER
ELECTRODES
PHILLIPS GAUGE
HEATING CURRENT
PIRANI GAUGE
WATER VAPOUR TRAP

FIG. 2·2

right angles to each other, while in the light profile method single lens is used for both illumination and viewing.

2.4 SILVERING TECHNIQUE:

For multiple beam interferometric and better microtopographical studies at higher magnification and resolution, the enhancement of the reflectivity of a surface is found to be necessary. This is done by coating a thin uniform film of silver on the surface by evaporating it under very low pressure (10^{-5} cm of Hg). This silver film does not disturb the topographical features on crystal surfaces. For evaporating silver films, a commercial evaporating unit of type 12EA manufactured by Edwards and Co., London was used (fig. 2.2). Hence the samples which are to be coated are kept on a stage, in the vacuum chamber, which is in the form of a large pyrex bell jar, 35.6 cm in height and 30.5 cm in diameter. This is connected through the tubing to an evacuating system consisting of a three-stage silicon oil diffusion pump, backed by a rotatory pump which produces the rough vacuum of the order of 0.2 mm of Hg. The diffusion pump as such, can be used only after rough or fore vacuum is created in the system. The backing (rough) vacuum and the final vacuum can be read directly on the Pirani gauge and Philips ionization gauge incorporated in the unit.

Silver is kept in a molybdenum filament or boat. When the pressure in the chamber falls to below 10^{-5} cm of Hg by diffusion pump, mean free path of silver molecule is more than a few diameters of chamber. When this pressure (10^{-5} cm of Hg) is reached, the boat is heated by a current of about 50 amps; the silver melts and starts evaporating. The filament is covered with an adjustable shutter in order to protect the substrate from receiving the vapour of the burnt impurities which can have a serious influence in increasing absorption. It is important to note that when the pressure falls below 10^{-5} cm of Hg, silver should be evaporated otherwise, there may be some spurious results due to small mean free path and moisture which directly affects the reflectivity and absorption of the thin film coated. It is known that water vapour and hydrocarbons present in the chamber seriously affect the quality of the film. Hence it is desirable that they should be removed from the chamber. Usually a petri dish containing fresh phosphorous pentoxide is kept in the chamber to absorb moisture, at the time of evaporation. The thickness of the silver film and hence the reflectivity is judged either by viewing filament from the top of the bell jar, or by calibrating the filament in terms of current and time of evaporation of silver.

The uniformity of the silver deposited is of paramount importance. The amount of condensation, in perfect vacuum from a point source, at any point on a plane surface is inversely proportional to the square of the distance of the point from the source and to the cosine of the angle between the normal to the plane and the line joining the point in question to the source. The distance between the source and the condensing plate is about 20 cm in the present case. It is found under the above mentioned conditions that the silver is deposited uniformly over the whole surface. It has been observed that the most stringent interference tests fail to reveal any serious variations in average silver thickness over such a surface, while no local variations can be detected at magnifications of about 400. To obtain high reflectivities of about 90%, the thickness of the film should be nearly 500 A°. Oil and impurities on the

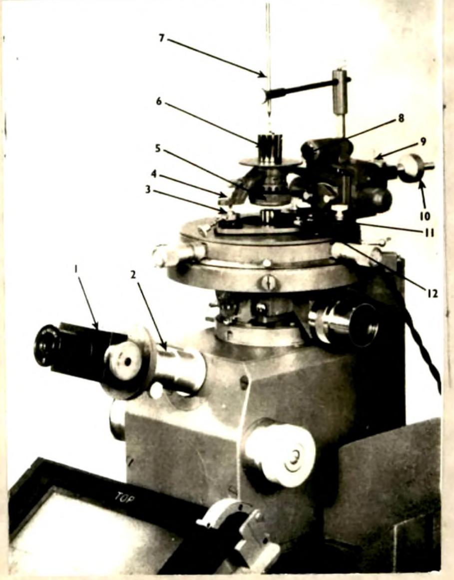

FIG. 2·3

surface to be silvered reduce the reflectivity coefficient somewhat, so a condition of cleanliness of surface is of vital importance.

2.5 INDENTATION TECHNIQUE:

The diamond pyramidal indenter equipment employed for the indentation work in the present study, is used with Vickers Projection Microscope. Fig. 2.3 shows the complete assembly of this equipment. The various parts are as follows:

1. Filar micrometer eyepiece in centering mount.
2. Tube length scale used for magnification setting.
3. Base plate contact anvil.
4. Beam contact tip.
5. Collet chuck securing specimen.
6. Calibrated weights used to apply load.
7. Load centre indicator.
8. Red signal lamp.
9. Auxiliary counter weights.
10. Counter weights.
11. Diamond indicator objective.
12. Electricity supply terminals.

The whole equipment (i.e. pivoted beam unit) is fixed to the stage plate of the microscope by means of two finger screws. On unscrewing these, it can be removed and placed to one side.

The support block for the load position is next removed on releasing the finger screw and is secured in the pocket at the back of the microscope slide.

The socket for the vertical pillar should be to the left hand side, as one faces the microscope. The vertical pillar, horizontal bar and central pin are assembled in position. The vertical position of the main bar is checked and if necessary adjusted by the use of the screw, which is afterwards locked by means of the grub screw provided.

The diamond indenter objective, assembled in its centering mount, is placed in position in the universal illuminator. Adequate care is taken to see that the objective is accurately centred to the optical axis of the instrument. Further the load position indicator pin is carefully lowered, taking care that its movement is truly vertical and its point centered over the diamond indenter. The horizontal bar is locked by its clamp screw and the set screw limiting the rotation of the vertical pillar is locked by its nut. The pin will now indicate the position of the indenter within the range of its vertical movement and may be clamped at any desired height just to clear off the weight placed on the beam plate. The electrical connection to the transformer or battery is then made to complete the circuit for the 4V (1.2W) lamp.

The specimen to be tested is mounted with either araldite or galva cement on a bakelite or aluminium circular disc (1 inch in diameter) to fit exactly in the collet provided. The surface to be tested should, of course, be normal to the axis of the cylindrical mount. The mounted specimen is then inserted into the collet and milled ring tightened with the aid of the double pin key until it is firmly gripped into the holder. The collet is then registered in the 'V' sideway and locked by means of the clamp screw. The filar micrometer (reading to 0.01 mm on the micrometer drum) in its centering mount is assembled and clamped to the end of the instrument eyepiece tube. The hinged lock screw should now be released and when electrical contact is made, the lamp will illuminate the red window.

The beam must now be balanced and this is accomplished by the removal or addition of counter weights in the packet provided and the adjustments of the counter weight of the screwed spindle. The vibration due to the fan etc. should be stopped, till the completion of the experiment, as the flickering of the indicator lamp is of great assistance while balancing for making the setting sensitive; i.e. the counter weights should be adjusted in such a way that contact can just be maintained. Under these conditions, the contact will break on gently tapping the main casing of the instrument with the fingers. The sensitivity in the present case was maintained for 100 mg.

Care is taken to see that the weights are placed just above the diamond indenter with the help of pre-set vertical pin indicating load position.

The selection of the load depends upon the material to be tested. Very light loads are used for soft materials or for minute crystalline structures. Generally, a load selected must give an impression of at least 10 μ diameter.

The region to be indented is scanned with the help of the reading objective and then the diamond indenter is placed properly in the centering mount. After ensuring that the fine motion mechanism is near the lower limit, the stage is lowered by course motion slide until the surface is approximately in focus and then clamping the slide. The fine motion mechanism is used to raise the indenter objective until the diamond makes contact with the specimen surface and lifts it sufficiently to break the contact between the conductors as denoted by the extinction of the red light. The speed of this fine motion drum should be maintained at 15 μ per second in order to maintain the static nature (basis) of the test. Strict count of the revolutions should be kept as fine motion is advanced; the clearance of the indenter should be 7 revolutions. The tube length should be kept at 242 mm and the contact of the diamond indenter with the specimen surface should be maintained for about 15 to 30 seconds (depending upon the test material). On reversing, the indenter speed should be the same (15 μ per sec.); then the indented region is examined by the reading objective through the filar eyepiece (total magnification X80).

When a series of indentations are to be made on a crystal surface, the distance between any two consecutive indentations should not be less than twice the length of the diagonal. In the present work this distance is kept eight times the diagonal length. The precaution is taken to prevent completely the interference of plastic flow due to consecutive indentations on a crystal surface.

It is important that the impression produced by the diamond pyramidal indenter, should be a square and if an error exists in the axial setting of the pyramid or the levelling of the sample to be tested, it should be checked first. The anisotropy of crystal surface may play a part and the impression may not be a square; then it should be symmetrical, i.e. it should be elongated along diagonal in a symmetrical fashion.

2.6 KYROPOULOS METHOD:

This method was named after Kyropoulas, who had established the technique in 1926. This technique is also known as 'crystal pulling' as it described the slow pulling of the crystal from the melt. Essentially a small single crystal seed is dipped into the surface of the melt and slowly withdrawn. By arranging the system so that the seed is slightly cooler than the melt; material solidifies in an ordinary manner on the seed as it is slowly withdrawn. 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. By this method large single crystals of potassium chloride were grown by the present author. Details of this method will be given in part III, Chapter VIII.

2.7 ETCH METHOD:

The crystal surfaces were etched by etchants in the usual manner, i.e. by dipping the crystal in an etchant of desired concentration for definite time period at a constant temperature and then washing it in running distilled water. It is known that the 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 the rinsing of the crystal.

The etching was carried out in [redacted] different ways, depending upon the temperature of etching viz. etching

(i) at room temperature (ii) at high temperatures and (iii) at low temperatures.

2.8 METHOD FOR MEASURING CONDUCTIVITY OF IONIC CRYSTAL:

For determining the electrical conductivity of materials, it is more customary to determine resistivity ρ measured in ohm-cm than conductivity ($\sigma = 1/\rho$). The resistivity can be measured either by using Ohm's Law or by Wheatstone's bridge principle.

For the present work LCR bridge (Toshniwal Instruments, Bombay) was used which is self contained impedance measuring system. It consists thermionic devices as active elements in the generator and detector circuits. The DC bridge supply is taken from the metal rectifier, which supplies about 8V limited by a resistor to a maximum of 80 mA.