PART – II

PART II

MICROHARDNESS OF CRYSTALS (GENERAL)

APPLICATION OF MEYER'S LAW AND KICK'S LAW
TO RHOMBOHEDRAL CRYSTALS : CALCITE AND SODIUM NITRATE

HARDNESS OF RHOMBOHEDRAL CRYSTALS :
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CHAPTER III

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3.1 INTRODUCTION:

Of all the mechanical properties of materials, hardness is the one which is least understood. It may be broadly defined as the ability of one body to resist penetration by another. It is by definition a relative property of a material and depends on the elastic and plastic properties of both the penetrated body and the penetrator. In addition, the comparative hardness of different materials is strongly dependent upon the method of measurement. All hardness tests measure some combination of various material-properties, namely, elastic modulus, yield stress (which denotes the onset of plastic behaviour or permanent distortion), physical imperfection, impurities and workhardening capacity. The latter is a measure of the increase in stress to continue plastic flow as strain increases. Since each hardness test measures a different combination of these properties, hardness itself is not an absolute quantity and, to be meaningful, any statement of hardness of a body must include the method used for measurement.

3.2 DEFINITIONS AND MEASUREMENTS:

From time to time many definitions have been given for hardness but none has been found to be satisfactory for quantitative interpretation of the processes taking place in indented materials. Tuckerman /1/ explained hardness as a hazily conceived aggregate or conglomeration of properties of a material more or less related to each other. The best general definition is given by Ashby /2/ "Hardness is a measure of the resistance to permanent deformation or damage." The general definition of indentation hardness which is related to the various forms of the indenters is the ratio of load applied to the surface area of the indentation. Meyer /3/ proposed that hardness should be defined as the ratio of load to the projected area of the indentation on the surface under consideration. Hence hardness has dimensions of stress. Spaeth /4/ suggested that hardness should not be defined as stress but as the resistance to indentation in the form of the ratio of the specific surface load to the unrecovered deformation. In short, the hardness of a solid is defined by the resistance which is a function of inner atomic forces /5/. Attempts towards a physical definition of hardness were made by Friedrich /6/, Goldschmidt /7/ and Chatterjee /8/.

Chatterjee defined indentation hardness as the work done per unit volume of the indentation in a static indentation test for a definite angle of indentation. On the basis of this definition and Meyer's law $P = ad^n$ for spherical indenters, he derived a formula for measurement of hardness. According to Plendl and Gielisse /9/ hardness can be defined as pressure or force per square centimeter of indented surface, and thus it can be conceived as an energy per unit volume, e.g. the ratio between the input energy and volume of indentation. They have concluded that resitance is a function of the lattice energy per unit volume and called it volumetric lattice energy (U/V) having the dimension ergs/c.c. U is the total cohesive energy of the lattice per mole and V is the molecular volume defined as M/S where M is a molecular weight and S is specific heat. The hardness was thus considered to be the absolute overall hardness. Matkin and Caffyn /10/ from their studies on hardness of sodium chloride single crystals containing divalent impurities, correlated hardness with the dislocation theory. They redefined hardness in terms of generation and/or movement of dislocations associated with indentation. It is the measure of the rate at which the dislocations dissipate energy when moving through a crystal lattice. It is now realised that (Westbrook and Conrad /11/) hardness is not a single property but rather a whole complex of mechanical properties and at the same time a measure of the intrinsic bonding of the material.

There are basically four methods to determine hardness of materials. They are as follows:

(1) Scratch hardness tester,

(ii) Abrasive method,

(iii) Dynamic method, and

(iv) Static indentation method.

Several books and review articles are available in which the information on hardness is partly or fully described/12-34/. They are briefly reviewed here.

(i) Scratch hardness:

An early method of measuring scratch hardness still in wide use today by mineralogists was developed by Friedrich Mohs in 1822. This gives a relative ranking of minerals based simply on their ability to scratch one another. The Mohs method is not suitable for a general use with materials of hardness greater than 4. Since in this range the intervals are rather closely and unevenly spaced. The modifications of this method were overshadowed by other sensitive methods and experiments.

(ii) Abrasive hardness:

Abrasive hardness is defined as the resistance to mechanical wear, a measure of which is the amount of material removed from the surface under specific condition. The hardness may be found by the depth of penetration.

(iii) Dynamic hardness:

The hardness measurement in this method involves the dynamic deformation of specimen under study and is determined by following considerations:

(a) Here, a steel sphere or a diamond-tipped hammer is dropped from a given height. The ball or hammer rebounds. The height to which it is rebound is read on a scale. This is taken to be the measure of hardness. The kinetic energy of a ball or hammer is used up partly in plastically deforming the specimen surface by creating a slight impression and partly in rebound. This test is sometimes referred to as 'dynamic rebound test'.

(b) Here, a steel sphere or a diamond-tipped hammer is dropped from a given height, the depth and size of the impression produced and the energy of impact are determined. The ratio of energy of impact to the volume of the indentation mark gives a measure of the hardness.

(c) Chalmers /35/ assessed the surface hardness in terms of the reduction in optical reflectivity when a known amount of sand was allowed to impinge on the surface under standard conditions.

(iv) Static indentation hardness:

The most widely used method of hardness testing is the static indentation method. This is the simplest and a very sensitive method in which a hard indenter (e.g., diamond) is applied slowly, and after a certain time of application, carefully removed, leaving behind a permanent indentation mark on the surface of specimen. Measurement is made either of the size of the indentation resulting from a fixed load on the indenter or the load necessary to force the indenter down to predetermined depth and the hardness of material is then defined as the ratio of the load to the area of the indentation mark. The hardness values so obtained vary with the indenter geometry and with the method of calculations.

Many combinations of indenter, load, loading procedure, and means of indentation measurement are used among the various tests in order to accommodate various shapes, sizes and hardness of specimens, and this has resulted in a proliferation of hardness scales. The most commonly used indenters are described in table 3.1. Diamond indenters must be used for hard materials in order to minimise errors due to elastic distortion of the indenter. In case ball indenters are used, the hardness number will be independent of load only when the ratio of load to indenter diameter is held constant. For cone and pyramidal indenters, hardness number will be independent of load for all loads above a certain minimum value depending upon specimen material.

3.3 GENERAL INFORMATION ON HARDNESS:

The hardness study undertaken, so far for studying the strength of solids and the effect of various treatments on the hardness of a solid, have proved somewhat useful. Most of the work has been reported on alkali halides and metals. Previously, hardness studies were made only from the view of materials research but as the expansion in the field of scientific research increased, the study on hardness helped in understanding various other mechanical properties of solids. Gilman and Roberts /36/ correlated indentation hardness with the elastic modulus by gathering the data for various materials. Their empirical linear relation shows that elastic modulus is an important factor which determines plastic resistivity against the dislocation motion. The behaviour of the indented region during the propagation of stresses which initiate dislocations and their motion is not yet fully understood. When an indenter is pressed on surface of a solid, the stresses are not simply tensile or compressive in nature. Stresses in various directions are set up and the one should treat the resultant plastic flow as a result of these combined stresses. It is also observed that the fundamental mechanisms of deformation can be either slip or twin or at times fracture.

(i) Slip is the most common mode of plastic deformation, which is characterised by the displacement of one part of crystal relative to another along certain definite crystallographic planes. The slip planes are usually of low indices and the slip directions are those of closely packed ones in a crystal structure.

(ii) Certain crystals may also deform by twinning, a mechanism by means of which a portion of a crystal may change lattice orientation with respect to the other in a definite symmetrical fashion. Schmidt and Boas /37/ described the twinning as the simple sliding of one plane of atoms over the next, the extent of the movement of each plane being proportional to its distance from the twinning plane. Partridge /38/ studied the microhardness anisotropy of magnesium and zinc crystals. He observed twin in above crystals and concluded that the resolved shear stress criterion is insufficient to account for the observed distribution of twins and any analysis which attempts to relate deformation twinning with hardness anisotropy must take into account the dimensional changes which occur during twin deformation. Indenting diamond flats with diamond indenter Phaal /39/ reported the slip and twinning of diamonds. Vahldick et al./40/, studied the slip system and twinning in molybdenum carbide single crystals with the help of Knoop and Vickers indenters. When the indented crystal was etched by a dislocation etchant, rosettes were formed on some crystals (usually alkali halides) indicating the dislocation distribution around an indentation. Dislocation loops are also formed around the indentation mark in ceasium iodide and sodium chloride 41,42/.

Many workers have proposed some or other explanation for the microcrack formation during indentation of a crystal surface. Smakula and Klein /43/ from their punching experiments on a sodium chloride explained the crack formation on the basis of shear on slip planes. Gilman /44/ attributed these microcracks which have a definite crystallographic direction to the piling up of dislocation on the slip plane. Breidth et al./45/, observed that crack formation is less at higher temperature (375°C) than at lower temperature (25°C). The cracks are usually observed to propagate from the corner of the impression.

The interferomatric studies of indented surfaces have revealed the nature of deformation and the history of the sample under test. Votava et al./46/ were the first to study the deformed region on the cleavage faces of mica and sodium chloride. Tolansky and Nickhols /47/ studied the indented surfaces of steel, tin and bismuth. They observed maximum distortion along the medians bisecting sides of the square and minimum along diagonals, showing thereby that no distortion projects beyond the diagonal. They established interferometrically that the symmetry in the fringe pattern is purely crystallographic and depends on the previous history of samples, and has nothing to do with the orientation of the square of indentation mark. They (1949) concluded that the convex sides, corresponding to extended wings in the interference pattern were 'piled-up' regions and concave sides were 'sinked-in' regions. Satyanarayan /48/ observed barrel or pin-cushion shape of indentation marks interferometrically, and gave idea about 'sinking-in' which occurs mostly at faces with very little along the diagonals of the indentation mark.

In crystalline materials plastic deformation or slip occurs through the movement of line imperfections called dislocations. As dislocations are multiplied (by one of several mechanisms) during deformation, their spacing decreases and they interact and impede each other's motion, thus leading to workhardening. The strength of dislocation interference depends on the nature of the crystal and on the ratio of temperature of deformation to the melting point of the crystal.

In general, hardening of crystals can be accomplished by introduction of any barrier to dislocation motion. This can occur by (a) workhardening, (b) impurity hardening (impurities tend to segregate to dislocations and pin them), (c) decreasing grain size in a polycrystal (grain boundaries are barriers to dislocation motion) (d) dispersion of fine particles of second phase in the crystal, and (e) phase transformations (by quenching).

It can be seen from this brief review that the amount of plastic deformation induced in a material by an indenter under load depends in a complicated way on a variety of factors which defy simple analysis.

3.4 VARIATION OF HARDNESS WITH LOAD:

For geometrically similar shapes of the indent marks for all loads, it can be shown that the hardness is independent of load. However, this is experimentally incorrect for certain ranges of applied loads. It is clear that during a hardness test the formation of indentation mark leads to an increase in effective hardness of the material and so the hardness number obtained is not actual hardness of the material in the initial state. This is mainly due to workhardening of the substance during the process of indentation which will be varying with the load. Attempts have been made to determine the absolute hardness by eliminating workhardening. This can be done only if the method does not appreciably deform the substance plastically. Absolute hardness was found to be one third of the normal hardness by Harrise/49/.

A large number of workers have studied the variation of hardness with load and the results given are quite confusing. Their findings are summarised below: Knoop et al. /50/, Bernhardt /51/, etc. observed an increase in hardness with the decrease in load whereas campbell et al. /52/, Mott /53/ etc. observed a decrease in hardness with decrease in load. Some authors e.g., Taylor /54/, Bergsman /55/ reported no significant change of hardness with load. In view of these different observations it has become rather difficult to establish any definite relationship of general validity between microhardness values and applied load.

There are two ways of studying relation between hardness (H) and applied load (P) or relation between load and diagonal (d) of the indentation mark. An empirical formula given by equation,

$$P = ad^n \quad \ldots \quad \ldots \quad (3.1)$$

where 'a' and 'n' are constants of the material under test.

The general definition of hardness number gives the relation

$$H_i = rP/d^2 \quad \ldots \quad \ldots \quad (3.2)$$

where 'r' is a constant and depends upon the geometry of the indenter, and 'i' indicates the method and indenter e.g., i = v, for Vickers hardness number. The combinations of the above equations yield,

$$H = a_1 d^{n-2} \quad \ldots \quad \ldots \quad (3.3)$$

$$H = a_2 P^{n-2/n} \quad \ldots \quad \ldots \quad (3.4)$$

where,

$$a_1 = ra \quad \ldots \quad \ldots \quad (3.5)$$

$$a_2 = ra^{2/n} \quad \ldots \quad \ldots \quad (3.6)$$

It has been shown that in case of Vickers hardness number, the value of the exponent 'n' is equal to 2 for all indenters that give geometrically similar impressions. This implies a constant hardness value for all loads.

Hanemann and Schulz /56/ from their observations, concluded that in the low load region 'n' generally has a value less than two. Onitsch /57/ found such low values of n (1 to 2) by observing variation of hardness with load while Grodzinski /58/ found variation of n values from 1.3 to 4.9. The standard hardness values thus obtained were expected to yield constant results but actual results obtained by different workers revealed disparities amounting to 30-50%. Due to this variation in the results, a high load region was selected which led to definition of microhardness independent of applied load. The hardness values so obtained for this region again showed scattered results even though the apparatus had a good mechanical precision. The scattered observations may be attributed to the following reasons:

(1) Equation, i.e., $P = ad^n$ is not completely valid.

(2) Microstructures exercise a considerable influence on measurements involving very small indentations.

(3) The experimental errors due to mechanical polishing, preparation of specimen, vibrations, loading rate, non-coincidence of microscope axis and applied load direction, shape of indenter, measurement of impression, etc., affect the hardness measurements considerably.

The term connected with the above test, microhardness means microindentation hardness, as it actually refers to the hardness measurement on the microscopic scale. Instead of the above term, some authors use low-load hardness. This confusion has arisen because these ranges have not been defined sharply. However, three possible regions can be defined as follows:

(1) Microhardness: From lowest possible loads upto maxinum of 200 gm.

(2) Low load hardness: Loads from 200 gm to 3 kg. The most characteristic region comprises of loads from 200 gm to 1 kg.

(3) Standard hardness: Loads over 3 kg.

Since the present study is made in the region of microhardness as defined in (1) above, the following presents a brief review of the work reported on microhardness of various crystals.

It is reported by many workers (1960 onwards) that hardness increases with load at low loads, attains a maximum value at a certain load, decreases and remains constant for a range of higher loads. Murphy /59/ studied hardness anisotropy in copper crystal; the variation in hardness by plastic deformation is shown to be in part due to the escape of primary edge dislocations.

Sugita /60/ while studying the indentation hardness of germanium crystal, found occurrence of ring cracks and radial cracks and that the load required to produce the observable cracks increased with the temperature. The temperature at which the microscopic slip lines become observable was higher in heavily doped crystals than in high purity crystals, indicating that dislocation multiplication was strongly affected by impurities.

Koserich and Bashmakou /61/ studied the formation of twins produced in Bi, Sb, Bi-Sb, Bi-Sn and Bi-Pb single crystals under action of concentrated load by diamond pyramidal microhardness tester. They showed that the length (l) of twins was proportional to the diagonal (d) of the indentation and the intensity of twinning is given by the coefficient in the equation-

$$l = a + \alpha d$$

The value of α was more for homogeneous alloys and increased with Sb content and remained constant for higher concentration of Sn and Pb.

The variation of hardness with load was also studied by Shah and Mathai /62/, who explained hardness in terms of slip taking place due to deformation in the crystal (tellurium). Edelman /63/ showed that microhardness of InSb and GaSb single crystals decreased exponentially with temperature. The presence of deflection points on the curves at 0.45 - 0.50 T_m indicate the deformation by slip. The activation energy for plastic flow in InSb and GaSb was estimated to be 0.6 eV.

Samsonov et al. /64/ studied temperature-dependence of microhardness of titanium carbide in the homogeneity range and found that the hardness decreases with decrease in carbon content in carbide. They also determined the activation energies of dislocation movement by plastic deformation.

Hardness variation was also studied with respect to the impurity content, dislocation density and the change in mobility of dislocation by various workers. Milvidski et al. /65/ observed decrease in hardness with increase in concentration of impurity and dislocation density in silicon single crystal. Kuz'menko et al. /66/ showed decrease in hardness due to change in mobility of dislocations as a result of excitation of electrons during lighting and their transition to higher energetic zone in titanium iodide and termed this a 'photochemical effect'. Beillin and Vekilov /67/ observed decrease in the hardness upto 60% illumination in Ge and Bi. Decrease in hardness was attributed to the induced photoconductivity, which altered the widths of the dislocation cores at the sample surface and in turn altered the plasticity.

Westbrook and Gilman /68/ studied electrochemical effect in a number of semiconductors. They observed decrease in resistance of semiconducting crystals to mechanical indentations in the presence of a small electric potential (0.05 to 10 V) between the indenter and the crystal surface. This was found to be due to significant enhancement of the surface photovoltage by a longitudinal electric field.

The variation of hardness in a number of semiconductors was studied in terms of concentration of charge carrier mobility and their interaction by many workers. Osvenskii et al. /69/ observed decrease in microhardness due to increase in carrier concentration for different contents of donor and acceptor impurities for GaAs and InSb smiconductors. In addition to this they also showed that decrease in hardness was independent of the type of carrier. Smirnov et al. /70/ studied the temperature dependence of carrier density and mobility of Ga crystals after irradiation with electrons and during various stages of annealing. They observed that the microhardness of such crystals did not recover fully their initial value and this was attributed to the interaction between radiation, defects and dislocations, which could act as sinks or condensations for compounds of Frankel pairs. Seltzer /71/ who studied the influence of charged defects on mechanical properties of lead sulphide found that the rosette wing length and hardness were nearly independent of concentration of free electrons in n-type, while it had marked dependence on concentration of holes in p-type. For a hole concentration about 8 x 10^{-7} cm^{-3}, rapid hardening was observed with attendant decrease in rosette size. It was suggested that this behaviour results from an e.s. interaction between charged dislocations and acceptor point defects.

Perinova and Urusovskaya /72/ studied the hardening of NaCl single crystals by X-rays and found the increase in microhardness by irradiation due to pinning of dislocations in irradiated samples and that the pinning was not destroyed by illumination. The effect of irradiation was also studied by Berzina and Berman /73/ who gave a relationship between the length of rays of etch figure star and proton irradiation dose in LiF, NaCl and KCl single crystal.

Because of substantial effect of surface layers on the microhardness, the increase in the microhardness was observed when applied load was reduced (Upit et al. /74/. They showed the ratio P/l^2 (where l is the length of rays in dislocation rosette around the indentation mark) was not constant (P against l^2 was not linear) at low loads due to retarding influence of the surface on the motion of dislocations. Further, they (1969) estimated the change of the mechanical properties of the crystal as the indentation depth decreased on the basis of correlation between the size of an indentation mark and the length of dislocation beam.

The distribution of dislocations around an indentation mark was studied using chemical etch pit technique by Urusovskaya and Tyagaradzhan /75/. They found larger number of prismatic loops. They examined the process of interaction of dislocations in crystals having CsCl lattice. Shukla and Murthy /76/ also studied the distribution of dislocations in NaCl single crystals. They found increase in the distance travelled by leading dislocations with increase in load. They further observed that impurity had little effect on the dimensions of the indentation but had a pronounced effect on length of the edge rays of the 'star pattern' and the ratio of the mean diagonal length to mean length of the edge rays was nearly constant. Matkin and Caffyn /77/ observed increase in the hardness with increase in Ca^{++} concentration in NaCl, while the distance travelled by leading dislocation was observed to decrease.

The effect of impurity on hardness was also studied by various workers. Dryden et al. /78/ studied the hardness of alkali halides when low concentration of divalent cations are incorporated in the crystal lattice on the basis of dielectric measurement of doped alkali halide crystals. They observed following effect of the state of aggregation of the divalent impurities on the critical resolved shear stress.

(1) the increase in critical shear stress was proportional to $C^{2/3}$, where C is the concentration of divalent ion-vacancy pairs,

(2) there was no increase in hardness as these divalent ion-vacancy pairs aggregate into groups of three (trimers),

(3) in NaCl : Mn^{++}, KCl : Sr^{++} and KCl : Ba^{++} there was no

increase in hardness as these trimers grow into large aggregates,

(4) in LiF : Mg^{++}, there was a large increase in hardness as the trimers grow into larger aggregates, and

(5) in NaCl : Ca^{++} the hardness increases as a second region of dielectric absorption appears. They have also concluded that the structure of the trimer was same in all these crystals and the trimer can grow in two ways, one of which produces an increase in the resistance to movement of dislocations. Urusovskaya et al. /79/ investigated the influence of impurity on the strength of crystals, microhardness, length of dislocation rosette rays and velocity of dislocation movement in CsI crystals. Takeuchi and Kitano /80/ reported the softening of NaCl crystal due to introduction of water molecules. The plastic resistance was almost dependent of dislocation velocity except at very high velocities. It was, however, strongly influenced by temperature, impurities, radiation damage and structure of core of dislocation. Gilman /81/ observed a sharp drop in plastic resistance of covalent crystals at roughly about two-third of the melting temperature and suggested that the drop was because the cores of dislocation in covalent crystal 'melt' at this temperature.

Temperature dependence of microhardness was also studied by Sarkozi and Vannay /82/. They concluded that besides thermal stress the observed hardening may be due to dislocations piled up at various impurities, to complexes in solid solution and vacancy clusters which were developed at high temperature. By quenching, the clusters become distributed in the crystals as fine dispersions.

Temperature dependence of microhardness was also studied by Shah /83/ who found that hardness of calcite cleavage faces increases with the temperature. Acharya /84/ found that the hardness of Zn and KBr decreases with the quenching temperature while the hardness of TGS increases with the quenching temperature.

Comparative study of Vickers and Knoop hardness numbers has been investigated in detail by Mohrnheim /85/ on metallic materials. An analysis of Knoop microhardness led Hays and Kendall /86/ to modify Meyer's /87/ law correlating applied load to the long Knoop diagonal by term which accounted for the resistance offered by the test specimens. Results were also discussed for usage of modified Meyer's law to obtain Knoop hardness numbers independent of applied load. Comparative study of Knoop and Vickers hardness numbers was also reported by Tietz and Troger /88/.

3.5 HARDNESS ANISOTROPY :

In principle, any kind of hardness test can be used to characterize the variations in the strength of materials in three principal directions of anisotropy. They could be the diamond pyramid indenter or even the spherical indenters, so long as the indentation load is sensitive enough to respond to the differences in the strengths of materials. If, however, the material has planar anisotropy, that is, the strength varies along different directions in a given plane, these symmetrical indenters can not be used to distinguish such property variations. One exception is the Knoop indenter: this was extensively used by the author to study hardness anisotropy of $NaNO_3$ and $CaCO_3$ cleavages.

Knoop and his associates originally developed the four-sided pyramid indenter for determining the hardness of semibrittle materials /89/. It was the unique geometry that offered several advantages over the conventional and symmetric indenters. For this reason, the Knoop hardness testing method has been extensively examined and put to use in different applications since its development in 1939 /90-94/. One of the features is that, because of its slow shallow depth of penetration, brittle materials like glass or minerals could be indented without causing premature fracture. Another feature is that, due to the nonsymmetric indenter shape, the variations in hardness along different directions in a given surface can be determined.

The geometry of the indenter is shown in Fig.3.1, where the included conical angles extending along the major and minor axes of the indenter are 172° 30' and 130°, respectively. The resulting impression on the surface of the test sample is also shown in Fig.1, where the major diagonal, L, is known to be about seven times longer than the minor diagonal, W. It is also generally assumed that there is negligible elastic recovery in the major diagonal direction compared to the minor diagonal direction when the indenter is removed /94/. Based on this assumption, the Knoop hardness number (KHN) is given as the indenter load divided by the indentation area projected on the original undisturbed surface in terms of the length of major diagonal and in units of kg/mm^2.

In addition to the problems associated with elastic recovery, the material near the indenter surface is known to pile up or sink in, depending on the interfacial frictional conditions and the material properties, such as the strain-hardening capacity /95/. This phenomenon also tends to change the mode of deformation near the indenter surface and therefore the hardness of material.

3·5·1 Orientation dependence of hardness:

An important feature of the Knoop hardness test is that the hardness value is dependent on the orientation of the major axis of the indenter in a given plane, as well as on the orientation of the plane itself with respect to the principal axis of anisotropy /90,91,93, 8-10/. Single crystals therefore can serve as ideal materials to establish the orientation dependence of hardness values.

One of the classic works along this line of investigation is by Daniels and Dunn /5/ on single crystal of silicon ferrite and zinc. They considered the magnitude of the KHN on a given surface as an inverse function of the ease with which slip could take place under the indenter. In essence, this was calculated by considering the force required to displace the material along the steepest slope of the indenter in terms of the resolved shear stress for a specific slip plane.

A cylindrical element of material by indenter with a cross-sectional area A, is shown schematically in Fig.3.2, where λ and ϕ are the angles measured from the loading axis to the slip direction and the slip-plane normal, respectively.

$$\text{Area of slip plane} = \frac{A}{\cos\phi}$$

$$\text{Component of force in the direction of slip} = F\cos\lambda$$

Hence critical resolved shear stress (CRSS) is given by-

$$\text{CRSS} = \frac{\text{Shear force}}{\text{Area over which the force acts}}$$

$$= \frac{F\cos\lambda}{A/\cos\phi} = \frac{F}{A}\cos\lambda\cos\phi$$

The above expression for resolved shear stress on the slip plane is further modified by a constraining factor, which is given as a measure of the maximum rotational effect on force along F specified between two axes AR (normal to slip direction) and H (normal to F and parallel to the indenter face). Given this angle, ψ, the resulting effective resolved shear stress (ERSS) is expressed as,

$$\text{ERSS} = \frac{F}{A}\cos\lambda\cos\phi\cos\psi$$

Brookes et al. have qualitatively established that when ERSS on a primary glide plane is minimum, the hardness is maximum and conversely. They had re-examined the above equation and presented a modified form as shown below:

$$\text{ERSS} = \frac{F}{A} \cos \lambda \cos \phi \; \frac{\cos \psi + \sin \gamma}{2}$$

where γ is the angle between a facet of the indenter and slip direction. It should be noted that the above angles are the ones made by different slip elements (slip plane, slip normal and axis of rotation of slip plane) with the indenter elements (stress axis F associated with a particular facet of the indenter and edge H of this facet parallel to the plane of indentation). The absolute values of F & A (area) can not be unambiguously determined in hardness studies/measurements. For constant F & A, ERSS is proportional to the cosine and sine terms as shown above. Hence a graphical analysis of variation of ERSS with orientation can be carried out. When the angles λ, ϕ, ψ and γ are known for each orientation A of major diagonal of Knoop indenter (with respect to the reference direction [100]). These angles vary with the rotation of the indenter with respect to reference direction [100]. Further the variations of angles is not universal but depends in a complicated way on the relative disposition of the slip elements around rotation axis of indenter. These will therefore be different from crystal to crystal and even in the same crystal from face to face.

For different orientations A, the evaluation of these angles is carried out by the stereographic method (SM) which is quite laborious, e.g., for one orientation and one facet of the indenter there are four angles to be determined. This will require four rotations of the stereogram. Hence for all four facets of indenter, there will be 16 rotations. If orientations of the indenter are taken in steps of 10° in a range of 0° to 90°, there will be 10 orientations and hence there will be 160 rotations of the stereogram corresponding to one slip system. If there are more than one symmetrically equivalent slip systems in a crystal, the number of rotations will be obviously very large. This will of course depend on the crystal, e.g., 480 rotations (= 160 x 3) are required for a rhombohedral crystal whereas 640 (= 160 x 4) rotations for an orthorhombic crystal. Accuracy of the SM is normally 2° and for polar regions it is still less. The author had taken help of computer to reduce this labour.

Thus visible traces of important crystallographic planes and angles made by them with important directions on a crystal surface under observation can be studied by SM, e.g., slip lines and twins represent the interaction of major crystallographic planes with surface under observation. Excellent account of SM are available in several books /99-102/. The salient features of this method is briefly described below.

Standard projection (0001) for calcite is available /99-102/. Since the present hardness work is on cleavage faces of calcite and $NaNO_3$, a standard projection of cleavage plane $\{10\bar{1}1\}$ was prepared from the projection (0001) available in the literature. The procedure for projecting a direction, say slip direction, on a stereogram is to select two planes from the standard projection $\{10\bar{1}1\}$ such that the required direction obeys zone law:

$$Hu + Kv + Lw = 0$$

where H, K, L $\equiv$ Indices of a plane, and

u, v, w $\equiv$ Indices of a direction,

e.g., for direction [011], u = 0, v = 1, w = 1 two planes (H_1 K_1 L_1) and (H_2 K_2 L_2) are to be obtained from the standard projection so that

$$H_1u + K_1v + L_1w = 0$$

$$H_2u + K_2v + L_2w = 0$$

In the present case the planes are $(01\bar{1}2)$ and $(\bar{2}\bar{1}10)$. The poles corresponding to these two planes are joined. They are on a great circle (same zone). From this zone, determine the zone axis direction in the usual way. This is the required direction. In this way projeections of various directions such as slip direction, slip plane normal and slip plane, axis of rotation, reference direction, etc., on the standard projection of cleavage plane are obtained. For indentation, load is applied vertically downward on a crystal surface. This gives rise to stress on the surface. There are two types of mutually perpendicular stresses (tensile and compressive). Tensile stress is parallel to a face of the indenter. The obtuse angle of the Knoop indenter is 172° 30', so half is 86° 15'. The direction of the longer diagonal of Knoop indenter is made to coincide with E-W direction by rotation and the point at 86° 15' is marked on the stereogram. This is the point or direction for tensile stress (F_T). The compressive stress F_C is along 90° to tensile stress direction. It is 3° 45' opposite to tensile stress direction from zero. Now projection of face-edge H, parallel to indenter face under consideration can be marked on the outermost great circle by drawing a line which is parallel to one of the faces of indenter and passing through the centre of the stereogram and meeting the great circle at a point. This point is H. For Knoop indenter H_1 and H_3 are similar; H_2 and H_4 are similar. For 10° rotation of the indenter, both F_T and H will rotate through 10° accordingly. After fixing the required directions on the standard projection, it is easy to determine angles λ, $\emptyset$, ψ and γ.

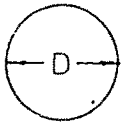
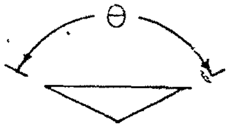
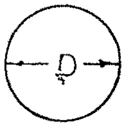
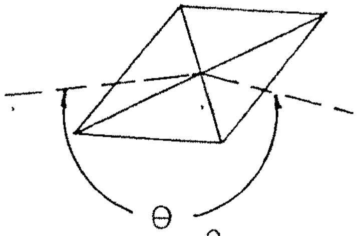
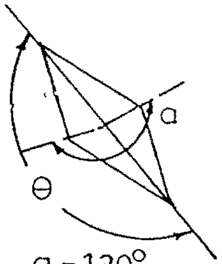
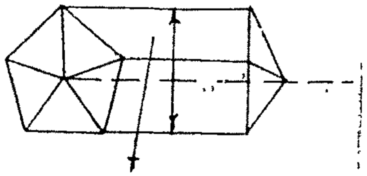
Then

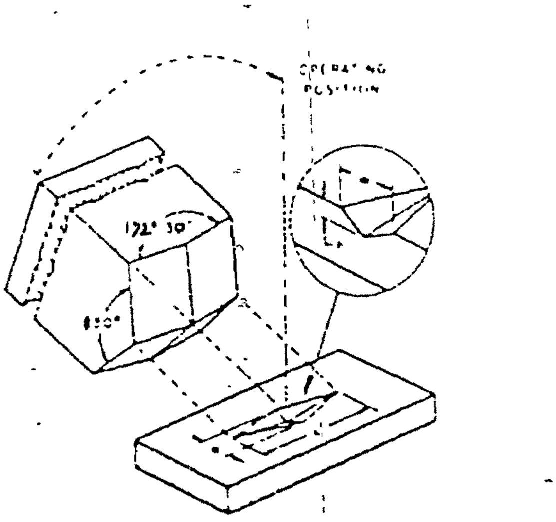
$$\cos\lambda \ \cos\emptyset \ \frac{\cos\psi + \sin\gamma}{2} = \frac{\mathrm{ERSS}}{(F/A)}$$

can be calculated.

The above represent a brief review of the work done on hardness of various crystals alongwith a stereographic method used to determine angles λ , ϕ, ψ & $\surd$ and hence ERSS. The present work is centred on the study of variation of load with diagonal length of indentation mark, variation of directional hardness with applied load on cleavage faces of synthetic sodium nitrate crystals grown from melt and of natural crystals of calcite at various quenching temperatures by using Knoop pyramidal indenter. Further the anisotropic nature of quench hardness was also studied for cleavage faces of the above crystals. This work is reported in chapters 4, 5, 6 and 7.

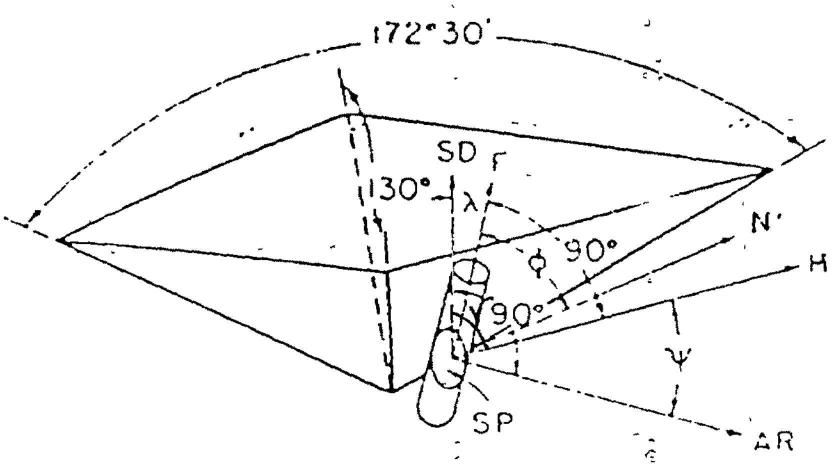
TABLE 3.1

	Brinell	**Rockwell**		**Vickers**	**Knoop**	**Brookes & Moxley**
Material of which indenter is made	Hardened steel or tungsten	Diamond	Hardened steel	Diamond	Diamond	Diamond
Shape of indenter	Sphere	Cone	Sphere	Square based pyramid	Rhomb based pyramid	Pentagonal
Dimensions of indenter	 D=10MM	 $\theta = 120^\circ$	 1/16 in 1/8 in. 1/4 in. 1/2 in.	 $\theta = 136^\circ$	 $a = 130^\circ$ $\theta = 172^\circ\text{-}30'$	 ZERO AZIMUTH
Characteristics	1. Geometrically similar impressions are not obtained.	1. Prepares the surface upon which the further penetration due to major load is based. 2. Hardness is read directly on the dial gauge. 3. Hardness value may be appreciable in error due to large amount of recovery along depth.		1. Geometrically similar impressions are obtained.	1. Hardness of uppermost surface layers can be found. 2. Sensitive to anisotropy of crystals. 3. Shorter diagonal undergoes recovery.	1. Eliminates the anisotropy normally observed in hardness with other indenters.



Some of the details of the Knoop indenter, together with its impression.

Fig. 3.1



Schematic diagram of the Knoop indenter and cylinder of deformation showing positions of force (F), slip direction (SD), slip plane (SP) and axes of rotation (AR and H)

Fig. 3.2

REFERENCES

1. Tuckerman, L.B., Mech. Eng. 47, 53-5, 1925.

2. Ashby, N.A., N.Z. Engng., 6, 33, 1951.

3. Meyer, E., Verdeutsch Ing., 52, 645, 1908.

4. Spaeth, W, Physik and Technique der haetre and Weiche, Berlin, 1940.

5. H. Tertsch, Z. Krist., 92, 39-48, 1935; Neus Jahrb. Mineral; Monatsh 73-87, 1951.

   Neus Jahrb. Mineral; Monatsh 136-44, 1952.

6. Friedrich, F., Portschrittec Chem. Physik, 18, 5-44, 1926.

7. Goldschmidt, V.M., Norske Vod Akad i Oslo Skr Mat Nat KI ∤ 8, P.102, 1926.

8. Chatterjee, G.P., Ind. J. Phys., 28, 9-20, 1956.

9. Plendl, J.N. and Gielisse, P.J., Phys. Revi., 125, 828-32, 1962.

10. Matkin, D.I. and Caffyn, J.E., Trans. Britt. Ceram. Soc., 62, 753-61, 1963.

11. Westbrook, J.H. and Conrad, H., 'The Science of Hardness and its Research Applications', American Soc. for Metals, Ohio, 1973.

12. Glazov V.M. & Vigdorovich, V.N., Microhardness of Metals and Semiconductors. (Translated from Russian by G.D. Archard) Consultants Bureau, 1971.

13. Holtz, H.A., On Hardness Tests of Metals and Metal Products, New York, 1937.

14. Ivanko A.A., Handbook of Hardness Data. (Translated from Russian by Israel Programme for Scientific Translations), Keter Press, Jerusalem, 1971.

15. Lea, F.C., Hardness of Metals. London, 1936.

16. Lysaght, V.E., Indentation Hardness Testing. Reinhold Publishing Co., N.Y., 1949.

17. Mott, B.W., Microindentation Hardness Testing. Butterworths Scientific Pubs., London, 1956.

18. O'Neill, H., Hardness of Metals and its Measurement. Chapman & Hall Ltd., London. 1967 (2nd Ed.)

19. Small, L., Hardness: Theory and Practice, Ferndale, Michigan, 1966.

20. Tabor, D., Hardness of Metals. Clarendon Press, Oxford, (UK) 1951

21. Williams, S.R., Hardness and Hardness Measurements, American Society for Metals, Cleveland, Ohio, 1942.

22. Kimura & Maddin, R., Quench Hardening in Metals, North Holland Pub. Co., Amsterdam, 1971.

23. Buckie, H., Progress in Microhardness Testing. Met. Rev. 4, 49, (1959)

24. Beeuwkes, R. (Jr), Plasticity & Fracture. Proc. Third Sagamore. Ordnance Mater. Res. Conf., 1956.

25. Lenhart, R.E., The Relationship of Hardness Measurements to Tensile & Compressive Flow Curve. WADC Technical Report No.55-114, Wright-Patterson Airforce Base, Dayton, Ohio, 1955.

26.. A.S.M., Metals Handbook. Cleveland, 1948.

27. A.S.T.M. Designation E-52T, Tentative Method of Test for Diamond Pyramid Hardness of Metallic Materials. 1952.

28. Desch, C.H., Metallography. London, 1937.

29. Field-Foster, P., The Mechanical Testing of Metals and Alloys. London, 1948

30. Kehl, G.L., The Principles of Metallographic Laboratory Practice. New York. 1943

31. Woolman, J., Sheet and Metals Users' Tech. Assoc. Conf. on Hardness Testing. 1953

32. Microhardness, its Theory and Practice with the Reichert Microhardness Tester. Wien, 1950

33. Chin, G.Y., Inhomogeneity of Plastic Deformation. American Society for Metals. 1973

34. Kehl, G.L., Seminar Amer. Soc. Metals. Modern Research Techniques in Physical Metallurgy. Cleveland. 1953

35. Chalmers, B., J. Inst. Metals, 67, 295-314, 1941.

36. Gilman, J.J. and Roberts, B.W., J. Appl. Phys., 32, 1405, 1961.

37. Schmidt, E., and Boas, W., Naturewise, 20, 416, 1955

38. Partridge, P.W., Nature, 203, 634-5, 1964

39. Phaal, C., Phil. Mag., 10, 887-91, 1964

40. Vahldick, F.W., Japan. J. Appl. Phys., 5, 663-70, 1966

41. Urusovskaya, A.A., Sov. Phys. Cryst. 10, 437-41, 1965

42. Kubo, K., J. Phys. Soc. Japan, 28, 117-87, 1970

43. Smakula, A. and Klein, M.W., Phys. Rev., 84, 1056, 1951

44. Gilman, J.J., Trans, AIME, 212, 783-91, 1958

45. Breidth, P., Greimer, E.S. and Eilise, W.C., Acta. Met., 5, 60063, 1957

46. Votava, B., Amelinckx, S. and Dekeysor, W., Physica, 19, 1163-72, 1953

47. Tolansky, S. and Nickols, D.G., Nature, 164, 840, 1949. Phil-Mag., 43, 410, 1952

48. Satyanarayan, B.S., Can. J. Teck., 3, 375-7, 1956

49. Harrise, P.W., J. Inst. Metals, 27, 1922

50. Knoop, F., Tech. Blatter, 27, 472-80, 1937

51. Bernhardt, E.O., Z. Metalkunde, 33, 135-44, 1941

52. Campbell, R.F., Henderson and Donleavy, M.R., Trans. Amer. Soc. Metals, 40, 954, 1948

53. Mott, B.W., 'Microindentation Hardness Testing' Butterworths Scientific Publications, London, Ch.1. 1956

54. Taylor, E.W., J. Inst. Metals, 74, 493-500, 1948

55. Bergsman, E.W., Metal Progress, 54, 183-88, 1948

56. Hanemann, H. and Schultz, F., Z. Metalkunde, 33, 124-34, 1941.

57. Onitsch, E.M., Microscopic, 2, 131-4, 1947

58. Grodzinski, P., Ind. Diamond Rev., 12; 209, 235, 1952

59. Murphy, R.J., Scripta Metallurgica, (USA) 3, 905-10, 1969

60. Sugita, Y., Japan. J. Appl. Phys., 10, 951, 1963

61. Koserich, V.M. and Bashmakov, V.I., Fiz. Metallovi, Metallevendenie, 9, 288-93, 1960

62. Shah, B.S. and Mathai, M.B., Current Sci. (India), 38, 4780, 1969

63. Edelman, F.L., Phys. Status Solidi (Germany), 7, K 65-66, 1964.

64. Samsonov, G.V., Kovalchenko, V.V., Dzemedinskii and Upadhyay, G.S., Fiz. Tekh., Paluprevachikov, 3, 1760-5, 1969

65. Milvidski, M.G., Osvenskii, V.B., Stolyarov, O.G. and Shylakov, D.B., Fiz. Metallovi, Metallovendenie, 20, 150-1, 1965

66. Kuz'menko, P.P., Novykov, N.N. and Ya. Horydko, N., Ukveyin, Fiz. Zn. (USSR), 8, 116-20, 1963

67. Beilin, V.M. and Vekilov, Yu.Kh., Fiz. Tverdogo, Tela, 5, 2372-4, 1963

68. Westbrook, J.J. & Gilman, J.J., J. Phys. Soc. Japan, 18, 15-19, 1963

69. Osvenskii, V.B., Milvidskii, M.G., Stolyarov, O.G. and Ivleva, V.S., Fiz. Tverdo., Tela, 10(9), 2809-11, 1968

70. Smirnov, L.S., Stas, V.F. and Khainovskaya, V.V., Fiz. Tekh. Paluprevachikov, 3, 1760-5, 1969

71. Seltzer, M.S., J. Appl. Phys., 37, 4780, 1966

72. Perinova, M. & Urusovskaya, A.A., Czech. J. Phys. B-6, 791-6, 1966

73. Berzina, I.G., Berman, I.B. and Savintsev, P.A., Sovt. Phys. Crst., 9, 483, 1965

74. Upit, G.P., Varchomiya, S.A. and Muktepavel, F.O., Fiz. Tverdo., Tela, 11, 2841-5. 1969

75. Urusovskaya, A.A. & Tyagaradzhan, R., Kristallographiya, 9, 531-6, 1965

76. Shukla, S.K. and Murthy, T.S., Nucl. Phys. and Solid State Phys. Symp.; Pawai, Bombay, (India), 1968

77. Matkin, D.X. and Caffyn, J.E., Trans. Britt. Ceram. Soc., 62, 753-61, 1963

78. Dryden, J.S., Morimoto, S. and Cook, J.S., Phil. Mag.(G.B.), 12, 379-91, 1965

79. Urusovskaya, A.A., Dobrzhanskii, G.F., Sizova, N.L. and Govorkov, V.G., Sovt. Phys. Cryst., 13, 6, 1969

80. Takeuchi, N. and Kitano, F., Japan. J. Appl. Phys., 10, 951, 1971

81. Gilman, J.J., Surface Chem. Metals and Semiconductor Symp.; John Wiley & Sons. N.Y. 1960

82. Sarkozi, J. and Vannay, L., Phys. Status Solidi, A, 6, (Germany), 39-41, 1971

83. Shah, R.T., Ph.D. Thesis, M.S. Univ. of Baroda, Baroda, 1976.

84. Acharya, C.T., Ph.D. Thesis, M.S. Univ. of Baroda, Baroda, 1978.

85. Mohrnheim, Prakt. Metallogr. (Germany), 10, 2, 94-97.

86. Hays, C. and Kendall, E.G., Metallography (USA), 6, 4, 275-82, 1973

87. Meyer, L., Quoted in 'The Science of Hardness Testing and its Research Applications', Am. Soc. for Metals, Ohio, 1973.

88. Tietz, H.D. and Troger, A., Feingeraete Tech. (Germany), 24, 8, 355-57, 1975

89. F. Knoop, C.G. Peters and W.B. Emerson, J. Res. Nat. Bur. Std., 23, 39 (1939)

90. H. Winchell, Am. Mineralogist, 30, 583 (1945)

91. N.W. Thibault and H.L. Nyquist, Trans. ASM, 38, 271 (1947)

92. L.P. Tarasov and N.W. Thibault, Trans. ASM, 38, 331 (1947)

93. F.W. Daniels and C.G. Dunn, Trans. ASM, 41, 419 (1949)

94. D. Tabor, The Hardness of Metals, Oxford University Press, 1951, P.100.

95. Ibid, P.15

96. C. Feng and C. Elbaum, Trans. AIME, 212, 47 (1958)

97. M. Schwartz, S.K. Nash and R. Zeman, Trans. AIME, 221, 554 (1961)

98. P.L. Rittenhouse and M.L. Picklesimer, Trans. AIME, 236, 496 (1966)

99. Tutton, A.E.H., 'Crystallography and Practical Crystal Measurements', Vol I (McMillan & Co. Ltd., London)(1922)

100. Barret, C.S., 'Structure of Metals' (McGraw Hill)(1953)

101. Bunshah, R.F., 'Techniques and Metals Research' Vol II, Part I (Interscience Publ.)(1968)

102. Dana & Ford, 'The System of Mineralogy', VII ed., Vol II, (John Wiley & Sons, Inc., N.Y.)(1952)