CHAPTER - VIII

MICROHARDNESS OF SnSe, SnS AND SnSe$_2$ SINGLE CRYSTALS
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MICROHARDNESS OF SnSe, SnS, AND SnSe₂ SINGLE CRYSTALS

This chapter reports the results obtained in the microhardness studies on SnSe, SnS and SnSe₂ single crystals. The Vickers and Knoop diamond pyramidal indenters have been used for the microhardness indentation tests on the cleavage planes (001) of SnSe and SnS and (0001) of SnSe₂ crystals. Part-A deals with the studies of hardness variation with applied load, temperature, time and azimuthal orientation of indenter. It also includes the effects of quenching, annealing and cold working on hardness. Surface anisotropy of hardness has been studied using Knoop indenter as well as the Vickers indenter. Results of these studies are discussed in this part of the chapter. Part-B deals with the study of indentation hardness creep. The results of dependence of hardness on indentation time and temperature have been used to determine the activation energy of creep.

PART-A

The method of indentation in hardness measurement is the most widely used method, primarily because it does not require large specimens and on a small specimen a number of measurements can be made. Indenters have been known to be either sharp or blunt according as their included angles are less or greater than 90°. As this angle increases, the indenter
tends to be blunt and the influence of friction and prior strain hardening
decreases. Also the value of constraint factor C in the relation between
hardness and yield stress i.e. \( H = CY \) tends to 3 as the effective cone angle
increases\(^{(1)}\). The stress field produced by such an indenter closely
approximates to the prediction of elastic theory. The Vickers diamond
pyramidal indenter used in the present study has included angle of 136°
which is a good compromise to minimize frictional effects and at the same
time to give a well defined geometrical similitude \([\text{square}]\) to the
indentation mark. Also for metal to diamond contact, the coefficient of
friction ranges from about 0.1 to 0.15 making the frictional effects less
pronounced\(^{(2)}\). The Vickers hardness is defined as the ratio of applied load
to the pyramidal contact area of indentation and turns out to be

\[
H_v = \frac{1854 \times P}{d^2} \quad \text{Kg/mm}^2
\]  

(1)

Where, \( H_v \) = Vickers hardness

\( d = \) mean diagonal of the indentation mark in \( \mu \text{m} \)

\( P = \) Applied load in gm

Similarly the Knoop hardness is defined as the ratio of applied load to the
contact area of of the rhomb based indenter:

\[
H_k = \frac{14230 \times P}{d^2} \quad \text{Kg/mm}^2
\]  

(2)

Where, \( H_k \) = Knoop hardness

153
\[ d = \text{major diagonal of the indentation mark in } \mu m \]
\[ P = \text{Applied load} \]

The crystals used for indentation test were all obtained by the Bridgman method at the speed of 4 mm/hr. The cleavage slices of thickness about 2 to 3 mm were obtained by cleaving the crystal at 0°C. Indentation tests under selected parameters were carried out at least three times, without changing azimuthal orientation of the surface and the average results are taken into account.

**VICKERS HARDNESS STUDY OF SnSe AND SnS CRYSTALS:**

To decide the loading time to be kept constant for the hardness tests at room temperature, experiments were performed for various loading times from 5 sec to 100 sec, keeping applied load constant at 80 gm which is a sufficiently high load for which the hardness was observed to be insensitive to small load variations.

Fig.1 and Fig.2 show the plots of the Vickers hardness \( H_v \) v/s Loading time \( t \), for SnSe and SnS crystals, respectively. It can be seen that the hardness is quite sensitive to loading times less than or equal to 25 secs as compared to higher loading times. Therefore for studying hardness variation with load, temperature and orientation, 30 sec was selected as the constant loading time. The indentations were performed at a very slow rate and for all indentations care was taken to see that the rate was nearly the
Fig. 1
same. Also, between two neighbouring indentation marks on the same surface, a separation of at least two indentations was maintained to avoid interference. The indentation mark produced was square in shape (Fig.3). The diagonals of indentation mark were measured using micrometer eyepiece. In the case of Vickers hardness measurement, the least count of the eyepiece was 0.125 micron while for Knoop hardness measurement, it was 0.816 micron.

HARDNESS DEPENDENCE ON LOAD:

Vickers hardness tests were carried out under different applied loads from 5 gm. to 100 gm at room temperature (300K). Fig. 4 shows the plot of Vickers hardness Hv v/s load P in the case of SnSe single crystals. Fig. 5 shows similar plot for the SnS single crystal. The plots indicate clearly that there is a complex dependence of Hv on load, particularly for loads less than 80 gm. In this low load range (LLR), the hardness exhibits an initial increase with load followed by a maximum. This maximum occurs around 30 gm for both the crystals. With further increase of load the hardness decreases and saturates at about 80 gm, while exhibiting an intermediate less prominent peak.

In respect of the above results, it should be noted that the hardness is known to vary considerably in the low load range as the work hardening capacity and elastic recovery of a particular material are dependent on the
load, the nature of surface indented and the depth to which the surface is penetrated by the indenter. For example, the low load hardness behaviour in the case of silicon single crystal has been explained on the basis of elastic recovery and piling up of material around the indentation mark\(^{(3)}\). Both the magnitude of work hardening and the depth to which it occurs are the greatest for the soft metallic materials which can be appreciably work hardened. Since the penetration depth at high loads is usually greater than that of the work hardened surface layer, the hardness value at high loads will be representative of the undeformed bulk of the material and hence independent of load. Thus, the room temperature hardness of SnSe and SnS single crystals are 100 Kg/mm\(^2\) and 97.5 Kg/mm\(^2\), respectively.

As has been pointed out, the nature of Hv v/s P plot in the LLR is characteristic of the phenomena occurring in the surface layers penetrated by the indenter. Now the depth of penetration depends usually on three factors:

1) The type of surface receiving the load which can again be divided into three categories:-

   a) Surface layer having different degree of cold working\(^{(4)}\)

   b) surface layer having finely precipitated particles\(^{(5)}\) and

   c) surface layer having different grain size\(^{(6)}\) and number of grains
indented\textsuperscript{(7)}, if the specimen is a polycrystal.

2) The magnitude of the applied load and

3) Accuracy in the normal operation of indenting the specimen and the rate at which the indentation is carried out, i.e., the strain rate. The time taken to realize the full load will evidently decide the strain rate.

All these factors play a prominent role when hardness tests are carried out by indentation at low loads. The surface layer-sensitive initial increase in hardness with load can be explained in terms of strain hardening based on dislocation theory. It is known that dislocations are surrounded by elastic stress fields. The stress fields of different dislocations interact strongly and lock the dislocations into metastable configurations. The effect becomes quite pronounced in metals where the dislocation mobility is usually high. Individual dislocations move readily at much lower stresses. The flow that occurs during indentation is therefore not limited by drag on isolated dislocations. The interactions between dislocations create jogs on them and these jogs create trails of dislocation dipoles behind the moving dislocations. As the penetration proceeds, the structure soon becomes filled with interacting dislocations forming complex networks resulting into efficient barriers to the motion of new dislocations. Further flow is then limited by the strength of interaction between the barriers and dislocations. The externally applied stress required to produce further plastic deformation
must be sufficient to make the dislocation move through the opposing stress fields of these interactions. The effective dislocated zones in the damaged layer causing such back stresses may correspond to what are known as "coherent regions".\(^{(8-9)}\)

The load dependence of hardness in LLR, Fig. 4 and Fig. 5, may be plausibly explained in terms of coherent regions. The presence of coherent regions has also been evidenced clearly by the depth profile of dislocation etch pit distributions below the indentations in the case of silver single crystals\(^{(10)}\). The coherent region in the present case accordingly extend to the depth of penetration of the indenter under the loads corresponding to the hardness peaks. Thus the increase in hardness with load in the low load range gets limited by the extent of the coherent region.

**EFFECT OF COLD WORKING:**

To study effect of work hardening on the load dependence of hardness in the LLR, the crystals were cold worked prior to indentation. For this purpose 5 to 6 mm thick cleaved plates of the crystals were placed between the two flat glass slabs and a load of about 3 kg was placed over the top slab. This effectively produced compression along the ‘c’ axis of the crystals. The compression was continued for 24 hrs. The experiments were conducted at room temperature. Then the crystals were cleaved to obtain one to two mm thick slices and the Vickers indentations were carried out at different loads. The experiment was conducted on a number of samples with similar treatment.
Fig. 6 shows average results of dependence of hardness $H_v$ on applied load $P$ for both the crystals. It is interesting to compare these plots with the plots in Fig. 4 and Fig. 5. In both the cases, i.e., SnSe and SnS, the peaks have shifted to lower loads in the case of the cold worked samples as compared to those obtained in the case of untreated crystals. This fact probably indicate that the extent of coherent region below the surface gets limited by the work hardening. In other words, due to cold working the over all dislocation net works increase in strength and number and produce barriers to generation and motion of new dislocation in the vicinity of the surface. Likewise, the saturation hardness, i.e., the load independent hardness has also increased to a considerable extent. In the case of SnSe, it has increased from 100 Kg/mm$^2$ to 130 Kg/mm$^2$ and in the case of SnS, it has increased from 97.5 Kg/mm$^2$ to 145 Kg/mm$^2$.

The Meyer's law is useful to analyse dependence of hardness on load. This law is $P = ad^n$ where the index $n$ is known as Meyer's index, and $P =$ applied load, $d =$ diagonal length of the indentation mark. whereas, $a =$ material constant. The deviation of the value of $n$ from 2 reflects the load dependence of hardness$^{(11)}$. The Meyer's law can be written as $\log P = \log a + n \log d$. Using the data of $d$ versus $P$, $\log p$ v/s $\log d$ plots were obtained.
Fig. 7(a) and Fig. 7(b) show the plots obtained from the data corresponding to Fig. 4 and Fig. 5, respectively, for SnSe and SnS crystals as cleaved. Fig. 8(a) and Fig. 8(b) are the plots obtained for cold worked crystals and correspond to the Hv v/s load P dependence shown in the Fig. 6. As can be seen, these plots are not single straight lines having unique slopes but rather they are each constituted of three lines with different slopes. Thus there are three values of Meyer index exhibited in the range of load used. These are given in Table-1, both for the un-treated and cold worked crystals.

The $n_3$ value of Meyer index corresponds to the high load range wherein the hardness is observed to be practically independent of load. These values are therefore about 2. It has been suggested that the Meyer index is greater than 2, if the hardness increases with load and this is the case with the $n_1$ values listed in the table. These values correspond to the range of low loads for which the hardness is observed to increase with load. It is interesting to note that the $n_1$ value for the cold worked crystals is greater than that for the untreated crystals.

Similarly the value of $n_2$ being less than 2 reflects the fact that the hardness decreases with load in the higher range of low loads. Further, like in the case of $n_1$, the value of $n_2$ is observed to be greater for the cold worked crystals than that for the untreated crystals.
Fig. 7(a)
Figure 8(a)
Fig. 8(c)
### TABLE-1

<table>
<thead>
<tr>
<th>Meyer Index</th>
<th>SnSe</th>
<th>SnS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As cleaved</td>
<td>Cold Worked</td>
</tr>
<tr>
<td>$n_1$</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td>$n_2$</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$n_3$</td>
<td>2.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>
EFFECT OF QUENCHING:

Raising temperature of crystals and quenching has an effect similar to work hardening. The crystals were raised to various high temperatures in vacuum and were maintained at respective high temperatures for about 36 hours. The vacuum sealed ampoule carrying the sample was then quenched by dropping it off the furnace into an ice-bath. The plots of \( H_v \) v/s \( P \) for various quenching temperatures are shown in Fig. 9 and Fig. 10 for SnSe and SnS crystals respectively. It can be seen in general that the hardness has increased with quenching temperature indicating the quench hardening phenomenon. The dependence of hardness on quenching temperature is known to follow a power law\(^{(12)}\)

\[
H T_Q^K = A
\]

where \( T_Q \) = Quenching Temperature

\( A \) and \( K \) = constants

\( H \) = load dependent hardness

The data obtained in the present study are in agreement with this relation. The plots of \( \log H_v \) v/s \( \log T_Q \) are shown in Figs. 11 and 12, for the SnSe and SnS crystals respectively. The lowest \( T_Q \) corresponds to room temperature (untreated).

The quench hardening indices, \( K \), obtained from the respective plots
Hardness $H_v$ (kg/mm$^2$)

<table>
<thead>
<tr>
<th>Load P (g)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>60</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
</table>

$T_Q = 873K$
$T_Q = 673K$
$T_Q = 473K$
$T_Q = 300K$

Fig. 9
Fig. 10

Hardness $H_v$ (kg/mm$^2$)

- $T_Q = 673 \, K$
- $T_Q = 623 \, K$
- $T_Q = 473 \, K$
- $T_Q = 300 \, K$

Load $P$ (gm)

174
Fig. 11
Fig. 12
are found to be about -0.8 and -0.9 for SnSe and SnS, respectively. It is interesting to observe how the hardness peak in the plots shifts with the increase in quenching temperature. Quenching has been known to bear its most pronounced effect on the crystal boundaries or surfaces. It can be seen from the plots that the hardness peak shifts towards lower loads as the quenching temperature increases, apart from overall increase in the hardness. In view of the above discussion, it follows that the coherent regions would get more and more confined to the vicinity of the surface with increase in quenching temperature, like in the case of cold working.

The general natures of load dependence of hardness in both the crystals are similar. The effect of quenching on the magnitude of hardness and on the extent of coherent region also follows similar trends in both the crystals. The quench-hardening index $K$ being a material constant, plots on the basis of the above equation were obtained by substituting $H$ by $H_p$, the peak hardness (Figs. 13 and 14). The slopes of these graphs again yield nearly the same value of $K$ as obtained by the plots in Figs. 11 and 12. The result highlights the significance of the hardness peaks in defining coherent regions. It is noteworthy that both of these tin chalcogenides are isostructural, with their lattice parameters equal within 4% and have similar bonds. Moreover, their forbidden gap energies also differ by 4%. With these comparable basic features, it should be noted that the bulk hardness values
are also equal within 4%. However, the empirical correlation between the band gap and hardness suggested for IV-V compounds\(^{(13)}\) does not hold true for these materials which are IV-VI compounds.

**HARDNESS ANISOTROPY:**

In order to study the anisotropy exhibited by the (001) planes of the crystals, the directional hardness was determined by producing indentations at various azimuthal orientations of the indenter with respect to the surface over a range of 0° to 180°. The reference 0° orientation was set as follows. It was observed while cleaving these crystals that apart from the wavy and irregular cleavage lines there were also some well defined rectilinear cleavage lines produced. In etching experiments such lines were found to be parallel to the etch pit rosettes obtained in the deformed specimens, both in the cases of SnSe and SnS crystals. These cleavage lines therefore ought to be in crystallographic directions. Hence these directions were chosen as reference directions along which the diagonal of the indentation mark was set to correspond to 0° orientation. The crystal was rotated about the indenter axis in steps of 15° while keeping applied load and loading time constant at 100 gm and 30 sec, respectively.

The plots of the measured hardness \(H_v\) v/s orientation \(\theta\) are shown in Figs. 15 and 16 for SnSe and SnS crystals. It can be seen that the hardness values repeat periodically at 90° intervals. Further, there are distinct maxima.
Fig. 15

Hardness $H_v$ (kg/mm$^2$)

Angle $\theta$ (degree)
Fig. 16

Hardness $H_v$ ($kg/mm^2$) vs Angle $\theta$ (degree)
and minima which are also periodic. Thus, in both the cases the hardness anisotropy corresponds to the four fold symmetry of the indenter. The crystals have two fold symmetry axis, normal to the cleavage planes, and hence parallel to indenter axis. Therefore in this case the symmetry of the indenter namely the four fold axis incorporates the symmetry axis of the crystals. The resulting symmetry in the hardness anisotropy thus does not distinguish the existence of two fold symmetry of the crystals. It is known that the resolved shear stress produced by the applied force on the slip systems in a crystal is a function of orientation of the force axis relative to the slip planes and directions. Therefore certain orientations are favourable for the indenter to produce deformation as compared to other orientations. In view of this, the hardness peaks observed above occur at such favourable orientations; whereas the minimum corresponds to the least favourable orientations. Maximum to minimum ratios of hardness are found to be 1.75 in the case of SnSe (Fig. 15) and 1.60 in the case of SnS (Fig. 16). Thus the degree of hardness anisotropy is nearly the same for these two crystals.

**VICKERS HARDNESS STUDY OF SnSe₂ CRYSTALS**

The indentation time in the hardness test is an important parameter, particularly for those materials which exhibit creep characteristics at ordinary temperatures. When studying dependence of hardness on load, orientation and temperature, the loading time should be kept constant. To
determine the loading time to be kept constant one should examine the time
dependence of hardness. Fig. 17 shows plot of $H_v$ v/s loading time $t$
obtained for this crystal. Compared to the cases of SnSe and SnS, the
hardness of this crystal is significantly less and at the same time it can be
observed from the above figure that the crystal exhibits a remarkable time
dependence of hardness. The hardness decreases with loading time and does
not saturate even up to a loading time as high as 60 sec. The hardness value
at around 50 to 60 sec corresponds to the indentation mark nearly the size of
the field of view of micrometer eyepiece. Therefore, the indentation mark
obtained at loading times more than 60 sec would not be measurable and
hence were not taken into account. In this situation, the choice of constant
loading of 50 sec to 60 sec would also be impracticable. Therefore a
compromise was made and a time of 15 sec was chosen, this being a
recommended loading time by the manufacturers of the hardness tester.

HARDNESS DEPENDENCE ON LOAD:

The plot of $H_v$ v/s applied load $P$ obtained at room temperature is
shown in Fig. 18. The nature of this plot is more or less similar to the plots
obtained for SnSe and SnS. The increase in hardness with load and
occurrence of hardness maxima could also be explained in the same way.
However, there is no saturation observed in this case up to the load of 150
gm, beyond which the size of the indentation mark exceeded the
Fig. 18

Load $P$ (g) vs. Hardness $H_v$ (Kg/mm$^2$)
measurement range. Nevertheless looking to the nature of high load tail of the graph a crude estimate of load independent hardness may be judged to be around 30 to 35 Kg/mm$^2$.

**EFFECT OF COLD WORKING:**

The crystals in the form of 2 to 3 mm thick cleavage slices were subjected to the room temperature compression treatment as described in the cases of SnSe and SnS crystals. Fig. 19 shows the average Hv v/s P plot for the cold worked crystals. This can be compared with the plot for the untreated crystals (Fig. 18). Apart from the overall rise of hardness values, the peak has shifted to a lower load. This aspect also follows the trend of SnSe and SnS and can be explained in terms of the coherent region which gets limited by the work hardening.

The constant, characterizing the load dependence of hardness, that is, the Meyer index n was obtained by plotting log P v/s log d. These plots are shown in Figs. 20 and 21, for untreated and cold worked crystals, respectively. It can be seen that these plots exhibit three linear regions in correspondence with the respective Hv v/s P plots in Fig.18 and 19. Accordingly the three slopes, i.e. the Meyer indices $n_1$, $n_2$ and $n_3$ are listed in Table-2. The $n_1$ values being greater than 2 indicate hardness increasing with load in the LLR whereas in the next two ranges of loads the values of $n_2$ and $n_3$ are less than 2 and hence indicate that the hardness decreases with increase in load.
Fig. 20
**TABLE-2**

<table>
<thead>
<tr>
<th>Meyer Index</th>
<th>As cleaved</th>
<th>Cold Worked</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_1 )</td>
<td>6.5</td>
<td>2.67</td>
</tr>
<tr>
<td>( n_2 )</td>
<td>1.71</td>
<td>1.67</td>
</tr>
<tr>
<td>( n_3 )</td>
<td>0.86</td>
<td>1.026</td>
</tr>
</tbody>
</table>
EFFECT OF QUENCHING:

The quenching treatment given to SnSe$_2$ crystals was similar to that in the case of SnSe and SnS crystals. Load dependence of hardness obtained for the untreated and quenched crystals is shown in Fig. 22. It can be seen that the hardness has increased with quenching temperature except for a small overlap around the peaks obtained for the two quenching temperatures 673 K and 873 K.

Since there is no saturation hardness observed up to the highest applied load, an estimate of this was obtained for each graph above, by extrapolating and following the trend of the high load tail of the graph. These estimates have been used to obtain the log $H_v$ v/s log $T_Q$ graph (Fig. 23), where $T_Q$ is the quenching temperature on absolute scale. The data is in fair agreement with the power law, i.e., equation (3). The quench hardening index obtained from this plot is $-0.8$.

HARDNESS ANISOTROPY:

The hardness anisotropy on (0001) plane (i.e. the cleavage plane) was obtained by indenting the surface at different azimuthal orientations of the surface relative to the indenter. The orientation range covered was from $0^\circ$ to $180^\circ$, where $0^\circ$ corresponds to the diagonal of the indentation mark, aligned parallel to the rectilinear cleavage lines as explained in the cases of SnSe and SnS crystals. The constant loading time was 15 sec and constant
Fig. 22
applied load 50 gm. The plot of $H_v$ versus orientation $\theta$ is shown in Fig. 24. The four fold symmetry of the indenter and six fold symmetry axis normal to the cleavage plane combine to result into twelve fold symmetry. This is evident in the above plot. The hardness values repeat at every $30^\circ$ interval. The ratio of maximum and minimum hardesses is obtained to be 1.20. This is less than the values obtained for SnSe and SnS crystals. This is expected because the SnSe$_2$ crystal has hexagonal structure which is quite more symmetric than the orthorhombic structures of SnSe and SnS crystals.

**KNOOP HARDNESS ANISOTROPY IN SnSe, SnS AND SnSe$_2$ CRYSTALS:**

Due to the characteristic geometry of the Knoop indenter it is specifically suitable to study the surface anisotropy in hardness. In particular the elongated rhombus shape of the indentation mark gives one of the two diagonal quite longer [about seven times] than the other$^{(14)}$.

Due to this it is efficient in revealing variation in hardness with direction on a given crystallographic surface. The author has used this indenter to determine the hardness anisotropy on the cleavage surfaces of SnSe, SnS and SnSe$_2$ crystals. As explained above in the case of Vickers hardness anisotropy, the zero degree orientation was referred to rectilinear cleavage lines. A load of 100 gm and indentation time of 30 sec in the case of SnSe and SnS crystals, while for SnSe$_2$ crystals load of 50 gm and 15 sec
indentation time were kept constant. Fig. 25, 26 and 27 give the plots of Knoop hardness $H_k$ v/s orientation $\theta$ for SnSe, SnS and SnSe$_2$ crystals, respectively. It can be seen that for SnSe and SnS crystals, the hardness values repeat at every $180^\circ$ intervals, thus revealing two fold symmetry resulting from the combined symmetries of the indenter and the indented surface. The ratio of maximum and minimum hardness values are about 2.33 and 1.70, respectively of SnSe and SnS crystals.

In the case of SnSe$_2$ crystal, the hardness value repeats at every $60^\circ$ intervals in accordance with the combined symmetries of the indenter and the indented surface. Further the ratio of maximum to minimum hardness values in this case is found to be 1.33.

It is interesting to note that the ratio of maximum to minimum hardness obtained, in the Knoop hardness anisotropy, is higher than that obtained in the Vickers hardness anisotropy in all the three crystals. Thus Knoop indenter is indeed more sensitive to anisotropy than Vickers indenter.

**PART - B**

This part reports the results obtained in the study of variation of microhardness with time at different temperatures of single crystals of SnSe, SnS and SnSe$_2$. The Vickers microhardness indentation tests were carried out on the cleavage surfaces of the crystals using a constant load and
Fig. 25
Fig. 26

Hardness $H_k$ (Kgf/mm²) vs. Angle $\theta$ (degree)

- 30
- 40
- 50
- 60
- 70

Angle $\theta$ (degree)
Fig. 27

![Graph showing the relationship between angle (degree) and hardness (kg/mm²).]
varying the time of indentation. The tests were repeated at different temperatures. The results obtained have been used to determine the activation energy for creep.

In assessing the strength of a crystal the indentation method assumes the hardness of a crystal to be independent of time after the load is fully applied. Infact, the indenter generally sinks into the crystal surface even after the application of full load. This is known as indentation creep. The use of indentation hardness is well known for the study of plastic yield properties of solids. The general behaviour regarding the decrease in the hardness with increasing loading time may be described by an empirical formula which incorporates the earlier relations given by the previous workers\(^{15-17}\). The behaviour of hardness is closely parallel to the creep characteristics of materials in unidirectional stress tests. Using a transient-creep equation derived by Mott\(^{18}\) for constant stress conditions and assuming that it can be applied even when the stress changes, Atkins et al\(^{19}\) analyzed the kinematics of creep process during indentation. They obtained good agreement between theory and experiment. Activation energy derived from the hardness measurements were close to the activation energies for self-diffusion. Their analysis suggested that inspite of its limited validity, a transient-creep equation of state may be used to describe the hardness behavior of solids at elevated temperatures.
The time dependence of plastic deformation [i.e. creep] plays a prominent role in hardness measurements. The nature and amount of plastic deformation and the measured hardness depend on temperature.

Recently in 1992, Fujiwara et al\textsuperscript{(20)} have studied the indentation creep in tin crystals which deform by pencil glide. The investigation was on the deformation mechanism of [001] pencil glide in the crystals at the temperatures 298 K, 333 K and 373 K. The steady state deformation due to pencil glide is rate controlled probably by cross slip between planes containing the [001] slip vector. Plastic deformation of single crystals of pure InP oriented for single glide has been studied in compression creep at 1068 K and 9 Mpa\textsuperscript{(21)}.

A. Ayensu et al\textsuperscript{(22)} have studied the power law creep of Cu wire specimens tested at temperatures 573 K, 673 K and 773 K under uniaxial stresses of 7.08, 14.16, 21.24 Mpa. The values of the stress exponent and activation energies indicated that the rate controlling mechanism for creep is grain boundary. A successful hardness-time relation in terms of temperature and creep activation energy has been given by Atkins et al\textsuperscript{(19)}.

The anelastic creep in Al-Zn was measured at room temperature by means of high resolution laser interferometer. The irreversible component of deformation qualified by measuring the visco-elastic after relaxation of Al-Zn has been studied as function of annealing time and temperature\textsuperscript{(23)}.
In this laboratory different workers have studied the time-dependence of microhardness on different crystals\textsuperscript{(24-27)}.

In view of the above, it was thought worthwhile to undertake the study of indentation creep of SnSe, SnS and SnSe\textsubscript{2} single crystals.

For the analysis of the data the well established relation given by Atkins et al\textsuperscript{(19)} was used. The relation is as under.

\[
H^{-3} - H_{0}^{-3} = A \exp\left(\frac{-Q}{3RT}\right) \left(t^{1/3} - t_{0}^{1/3}\right)
\]

where,

\(H\) = the hardness value at time \(t_{0}\),

\(H_{0}\) = the hardness value immediately after attaining the full load \(P\) at time \(t_{0}\),

\(t\) = time

\(Q\) = Activation energy for creep

\(R\) = the gas constant

\(A\) = Constant

\(T\) = Absolute temperature

This simplified equation has been used to determine the activation energy for creep. The equation can be written in a convenient form as

\[
\ln \left( H^{-3} - H_{0}^{-3} \right) = \ln A + \ln \left( t^{1/3} - t_{0}^{1/3} \right) - Q / 3RT
\]

All the observations were obtained on freshly cleaved basal faces of
these crystals, using Vickers pyramidal indenter. A constant load of 100 gm was used, for which the hardness of SnSe and SnS crystals were found to be virtually independent of load, while 50 gm constant load was used in the case of SnSe₂ crystals. The indentation of the specimen were carried out at 303 K, 328 K, 333 K, 363 K, 385 K and 388 K and the indentation time was varied from 5 sec to 80 sec at each temperature. The temperature could not be exceeded beyond 388 K since there is no provision of heat-shield on the hardness tester to prevent possible damage of indenter-objective at high temperature.

It has been observed that when all parameters are kept constant, the microhardness decreases with increasing temperature. Fig.28 shows the plots of \( \ln H_v \) v/s \( T / T_m \) which are straight lines for SnSe, SnS and SnSe₂ crystals. In all these cases the indentation time was 30 sec. In above graph \( T_m \) is the melting point of the crystal [SnSe -1133K , SnS - 1154K and SnSe₂ - 930K]. The nature of the graph shows that the hardness of the crystals decreases with increase of temperature. Similar decrease in hardness was found in the cases of Si, Ge and Cu crystals.(28).

The experimental observation needed to calculate \( Q \) are shown in the form of \( \ln H_v \) v/s \( \ln t \) plots in Figs. 29 (a), (b) and (c) respectively for SnSe, SnS and SnSe₂ crystals. These are straight lines obtained at different temperatures indicated near each graph for SnSe, SnS and SnSe₂.
Fig. 28(a)
Fig. 28(b)
In H
5-6
5-2
>4-8
4-4
12 3 4
int
Fig. lfta)
208

<table>
<thead>
<tr>
<th>NO.</th>
<th>TEMPERATURE [K]</th>
<th>HARDNESS H₀ [KG/mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>303</td>
<td>330.30</td>
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<tr>
<td>2</td>
<td>333</td>
<td>311.06</td>
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<tr>
<td>3</td>
<td>363</td>
<td>287.15</td>
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<tr>
<td>4</td>
<td>388</td>
<td>275.89</td>
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</table>

Fig. 29 (a)
\[ \ln H_V \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>TEMPERATURE [K]</th>
<th>HARDNESS ( H_0 ) [KG/mm²]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>181.27</td>
</tr>
<tr>
<td>2</td>
<td>328</td>
<td>162.39</td>
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<td>3</td>
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<td>148.41</td>
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<tr>
<td>4</td>
<td>385</td>
<td>130.32</td>
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</table>
respectively. From the nature of the graphs it is clear that the lnHv varies linearly with ln t. It has been predicted by Atkins et al\(^{(5)}\) that the negative slope of such straight lines should increase with increasing temperature. However, the present author is unable to draw any such conclusion, due to limited range of temperatures used.

The values of H\(_0\) at time t\(_0\), selected as one second, was obtained by extrapolating the straight lines to ln t = 0 and the intercepts on ln Hv axis, gives the values of H\(_0\) for the different temperatures. Using these values of H\(_0\) and t\(_0\), H\(^{-3}\) - H\(_0\)^{-3} and t\(^{1/3}\) - t\(_0\)^{1/3} were calculated and also plotted as shown in Fig. 30 (a),(b) and (c), respectively for SnSe, SnS and SnSe\(_2\) crystals. From these plots, it is clear that all the straight lines have nearly equal slopes as predicted by equation (2). The value of activation energy Q for creep was calculated by finding the difference between the intercepts at two temperatures T\(_1\) and T\(_2\) in these graphs and equating them to

\[
Q = \frac{1}{3R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Thus if T\(_1\) is selected as 304 K, T\(_2\) can be either 333 K, or 363 K or 385 K. The calculations were made considering all combinations of T\(_2\) and T\(_1\) and average value of Q was found for each of the crystals. The activation energies Q thus obtained for SnSe, SnS and SnSe\(_2\) crystals are listed in Table 3.
\[ \ln \left( \frac{H - H_0}{3} \right) + 1 \]

\[ \ln \left( \frac{1/3 - t_{1/3}}{1/3} \right) + 1 \]

**Table**

<table>
<thead>
<tr>
<th>NO.</th>
<th>TEMPERATURE [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>363</td>
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<td>388</td>
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**Fig.30(a)**
Fig. 30(b)

<table>
<thead>
<tr>
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</tr>
</thead>
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<tr>
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<tr>
<td>3</td>
<td>363</td>
</tr>
<tr>
<td>4</td>
<td>388</td>
</tr>
<tr>
<td>MATERIAL</td>
<td>ACTIVATION ENERGY FOR CREEP (Q) K Cal / Mole</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>SnSe</td>
<td>2.92</td>
</tr>
<tr>
<td>SnS</td>
<td>1.75</td>
</tr>
<tr>
<td>SnSe₂</td>
<td>2.04</td>
</tr>
</tbody>
</table>
In some cases, the activation energy for creep has been found to be
different for different temperature ranges\(^{29-30}\) and an alternate method for
evaluating Q is to be sought, but since the temperature range in the present
study is not too large, the author assumes the value of Q to be constant with
temperature in the range employed. This assumption has been confirmed by
Bhatt and Desai\(^{(25)}\), R.C.Shah\(^{(24)}\) and T.M.Jani\(^{(27)}\) in their study of InBi, Bi\(_x\)Sb\(_x\) and InBi\(_{1-x}\)Te\(_x\) single crystals, respectively.

CONCLUSIONS:

1. Microhardness is a load dependent quantity and the variation is quite
prominent in low load ranges and only for sufficient high applied loads it
becomes virtually independent of load.

2. The hardness peaks observed in \(H_v\) V/S load p plots may be explained in
terms of deformation induced coherent regions.

3. Due to work hardening, the crystal hardness increases. The Meyer index
is not truely constant but may be different in different load ranges.

4. The orientation dependence of hardness conforms to the symmetry axis
normal to the indented surface. The Vickers indenter measures nearly
the same surface anisotropy in SnSe and SnS crystals, whereas it
indicates the SnSe\(_2\) crystal to be quite less anisotropic. Similar results
obtained with Knoop indentor indicate pronounced anisotropy in all the three crystals.

5. The indentation creep behaviour of the crystals approximates to the relation given by Atkins et al. The creep activation energies in the temperature range used have been found to be about 2.92 Kcal/mole, 1.75 Kcal/mole and 2.04 Kcal/mole for SnSe, SnS and SnSe$_2$, respectively.
REFERENCES :


18. Mott N.F., Phil. Mag., 44(1953)742.


