CHAPTER 3

EXPERIMENTAL METHODS

The experimental methods used to obtain the kinetics data, under isobaric-isothermal conditions, of the \( \alpha \rightarrow \omega \) transformation in Ti, fcc \( \rightarrow \) bcc transformation in Yb, and the crystallization in the solid state of amorphous selenium (a-Se) are described in this chapter. The data up to 10 GPa for Ti and 4.6 GPa for Yb at room temperature were obtained by monitoring the time dependence of the resistance change at the transformation using an opposed anvil apparatus. The data for Se were obtained by monitoring the time dependence of the volume change at the a-Se \( \rightarrow \) trigonal Se transformation using the piston displacement method, and also by the microscopic observation on the quenched partially crystallized samples.

In order to set the isobaric conditions, it is important to know the specimen pressure \((p)\) versus the applied pressure \((p_N)\) relation accurately. This relation is easily determined in the piston-cylinder apparatus since the specimen pressure can be calculated knowing the force and area. The frictional losses in the applied force can be minimized experimentally, and estimated from measurements.
carried out with both increasing and decreasing loads.

In the opposed anvil apparatus, the $p-p_N$ relation has to be obtained by the use of either secondary pressure gauges or fixed points on the pressure scale. The $p-p_N$ relation should be critically examined for reproducibility, and a knowledge of the factors affecting this relation is essential. The dimensions of the gasket and pressure transmitter discs have to be optimized in order to obtain a reasonable pressure amplification, and at the same time a uniform pressure distribution within the cell. These considerations led to the development of a high pressure resistivity cell suitable for the kinetics studies of polymorphic transformations in metallic and semiconducting specimens up to 10 GPa.

3.1 High pressure system

3.1.1 Hydraulic press

The 100 ton hydraulic press used in the present studies (Fig.3.1) consists of a pump delivering pressure to a hydraulic ram nearly 5 inches in diameter. The pump can be operated both manually and by an electric motor. The ram fixed on a frame drives the platen $P_1$ and loads the opposed
Fig. (3. 1). 100 ton hydraulic press; $P_1$-movable platen, $P_2$-fixed platen.
anvil system (with the high pressure cell in between) by pressing it against a fixed platen \( P_2 \) supported by four tie rods. The oil pressure is read on a Heise gauge to a precision of 2 bars. A pressure transducer (0-500 bars) connected in line with the hydraulic ram is used whenever a continuous record of the oil pressure is required. Four compressible springs mounted along the tie rods between the platens \( P_1 \) and \( P_2 \) enable the smooth retraction of the ram.

3.1.2 **Opposed anvil system**

The opposed anvil set-up useful up to 10 GPa is shown in Fig.(3.2). This consists of a pair of tungsten carbide anvils with 6 per cent cobalt binder. The anvils are 25 mm in diameter and 40 mm in length; the cylindrical surface has a \( 1^\circ \) taper. The anvil face, a truncated right circular cone, has a diameter 12.5 mm. The angle of the taper is nearly \( 7^\circ \). For lateral support, the anvils are press-fitted in 17-4-PH steel binding rings (age hardened to nearly 40-50 Rockwell C) with an interference of 1 per cent. In an actual experiment, the anvils are backed by tungsten carbide blanks press-fitted in steel binding rings.
FIG. 3. Tungsten carbide anvils press-fitted in 17.4-PH steel blinding rings.
3.1.3 High pressure resistivity cell used in pressure calibration

The high pressure resistivity cell with a typical sample assembly in a four-lead configuration is shown in Fig.[3.3(a)]. The stacking sequence of the various components of the cell is shown in Fig. [3.3(b)].

The cell consists of a stack of two compressible gaskets (p,p). Grooves are made in one of the gaskets to accommodate the electrical leads (a fine copper wire 100 μm in diameter). This gasket is kept in position on one of the anvils, and held in place by a small quantity of Duco cement applied at the outer edges of the gasket. A pressure transmitter disc T is placed in the central hole of the gasket. The specimen is placed on the disc T, and the copper leads are arranged in the respective grooves which prevent the pinching of the wires. The second gasket is kept atop the first and held in place by a small quantity of Duco cement on the outer edges of the gaskets. The remaining space in the cell is filled by a second pressure transmitter disc. The other anvil is placed on the cell and held in position by an aligning ring. The anvil-assembly is transferred to the hydraulic press, and kept in position.
Fig. (3.3). (a) High pressure resistivity cell with the sample in a four-lead configuration. (b) Stacking sequence of the various components of the cell: P,P - pyrophylite gaskets, T,T - pressure transmitter discs, S - specimen, C₁,C₂-current leads, L₁,L₂-voltage leads.
between the back-up plates made of press-fitted tungsten carbide. The hydraulic ram is raised using the motor pump until the anvil system makes contact with the top platen \( \rho_z \), and then the assembly is pressurized gradually by manually working the pump.

3.1.4 Gasket and the pressure transmitter

Pyrophyllite was used as the gasket material. The outer diameter of the gasket was fixed at 12.5 mm (equal to the diameter of the anvil face). The gasket had a central hole 5 mm in diameter to accommodate the pressure transmitter discs, the sample and the electrical leads. The diameter of the central hole was fixed at 5 mm mainly because of the convenience of operation. The thickness of the gasket was generally 0.8 mm unless otherwise specified. This value of the thickness was derived from extensive experiments designed to map the pressure distribution within the gasket.

The gaskets made of natural pyrophyllite undergo extensive plastic flow during the initial loading. Prefiring treatment is known to affect its mechanical properties [108], and improve its performance. The gaskets fired at
800°C for 4 hours were found suitable for the present experiments.

Talc, epoxy and AgCl were tried as pressure transmitters. The performance of the high pressure cell was assessed by using each of these as a pressure transmitter in the calibration experiments. The diameter of these discs (two in each run) was 5 mm, and the total thickness was 10 per cent less than the gasket thickness. Initially, when the load \( F \) on the area \( A \) of the anvils is small, the nominal pressure \( F/A \) is less than the yield strength \( Y_S \) of the pyrophyllite gasket. When \( F/A \) exceeds \( Y_S \), the gasket plastically deforms and extrudes from the anvil region. The friction between the gasket and the anvil opposes the plastic flow. With further increase in load, the plastic flow of the gasket decreases and the gasket undergoes an elastic compression. In this condition, the uniaxial stress approximates to hydrostatic pressure \( [109] \). The under-loading introduced ensures that the sample experiences the load mostly after the gasket is formed.

The talc discs were machined from solid lumps. The silver chloride discs were machined from powder compacts. Silver chloride was found to react with some of the
specimens used for the high pressure studies, especially Yb. In such cases, the reaction was prevented by separating the AgCl discs from the specimen by thin teflon discs (thickness 20 \( \mu \text{m} \)) punched from tapes. The epoxy discs were punched out from epoxy (CY 212 resin and 10 per cent by weight HY 951 hardener, Ciba India Ltd) sheets nearly 0.5 mm thick. It was noticed [110] that the epoxy discs soften considerably on soaking them in a methanol-ethanol (4:1) mixture, resulting in improved pressure transmission. The epoxy discs were, therefore, soaked in the methanol-ethanol mixture for 30 minutes before loading them in the cell.

The pyrophyllite gaskets and the pressure transmitter discs were machined to the required diameter with an accuracy of \( \pm 0.01 \) mm. The gasket thickness was larger than required, and were hand ground to the required value with a tolerance of \( \pm 0.01 \) mm. This precise control over the dimensions resulted in reproducible \( p-p_N \) relation. This aspect will be further discussed in Sections 3.3 and 3.4.

3.2 Resistance measurement and data recording

The resistance of the specimen, typically 5 x 0.5 x
0.05 mm, was measured using the four-lead arrangement [Fig. 3.3(a)]. A constant current source was used to maintain a current of about 10 mA through the specimen S. The wires $C_1$ and $C_2$ served as current leads. The output across the voltage leads $L_1$ and $L_2$ was connected to a high sensitivity (1 $\mu$V) Rikadenki strip chart recorder. A continuous record of the output voltage and therefore the resistance of the sample were obtained with a continuously increasing load. When the change in specimen resistance was smaller than that could be detected by the above method, a Leeds and Northrup potentiometer (K5) was used to measure the voltages with a precision of 20 nV. The sensitivity in the resistance measurement using the recorder was 1 part in $10^3$, whereas with K5, it was 2 parts in $10^5$.

3.3 Pressure calibration

The $p_{N}$ relation was obtained on the basis of fixed points, Bi I$\rightarrow$II (2.55 GPa), Tl II$\rightarrow$III (3.67 GPa), Ba I$\rightarrow$II (5.5 GPa), Bi III$\rightarrow$V (7.7 GPa). The figures in the parentheses are the transformation pressures at room temperature.

The high pressure resistivity cell shown in
Fig. (3.3a) was used, the thickness of the gasket being 0.8 mm and that of the talc discs 0.72 mm. Lumps of Bi (99.999 per cent pure), Ba (99 per cent) and Tl (99.9 per cent) were flattened, and from these, the specimens measuring 5 x 0.5 x 0.05 mm were cut. Separate experiments were performed with each of these as the test sample. The distance between the voltage leads $L_1$ and $L_2$ was typically 1.5 mm. The nominal pressure was continuously increased at a rate 0.07 GPa min$^{-1}$, and the output voltage across the leads $L_1$ and $L_2$ (for a constant current through the sample) was continuously recorded. The nominal pressure ($p_N$) at which the transformation was first seen to occur was noted. The specimen was continuously loaded at the same rate till the transformation was complete, and a desired value of pressure after the transformation was reached.

It has been recommended [29,30] that for pressure calibration in solid media apparatus, the transformation pressures (listed above) may be assigned to the forward transformation start pressure. Following this, the $p-p_N$ relation was obtained, and is shown in Fig. (3.4). It is seen that the $p-p_N$ relation is linear, and the line passes through the origin. The pressure amplification factor
Fig. (3. 4). Specimen pressure as a function of the nominal (applied) pressure.
\( p/p_N = p_A \) is nearly 2.35. The data points shown in Fig.(3.4) correspond to mean values of \( p_N \) obtained from a number of independent runs; the standard deviation in the values of \( p_N \) is nearly 6 per cent. The error bars indicate the uncertainty in the sample pressure when it is determined from the mean \( p-p_N \) line. These errors are presumed to arise from two factors: (1) irreproducibility of the thickness of the gaskets and the talc discs at levels less than 0.01 mm (2) uncontrollable variation in the mechanical properties of pyrophyllite and talc from one batch to another. The method used to further reduce this uncertainty in the specimen pressure is discussed in Section 3.5.

It was observed that in spite of the 6 per cent variation in \( p_N \), the linearity of the \( p-p_N \) relation was not affected. Based on this, the relative resistance-pressure data of Bi, Tl and Ba were obtained. The sample pressure \( p \) was calculated by taking the value of \( p_N \) at the start of the transformation to correspond to the respective transformation pressure. These data are shown in Fig.(3.5). For these materials, the observed values of the resistance change prior to and at the transformation are in reasonable agreement with the data available in literature.
Fig. (3.5). Resistance vs. pressure data of a) bismuth, b) thallium, and c) barium at room temperature. $R(0.5)$ denotes the resistance at 0.5 GPa.
It was observed that the width of the transformation increased when the distance $L_1 L_2$ between the voltage leads [Fig. (3.3a)] was increased beyond 1.5 mm. This is due to the radial pressure gradients which are invariably present when a solid is used as a pressure transmitter in the opposed anvil apparatus. The estimation of the radial pressure gradients requires the mapping of the pressure distribution in the cell.

3.4 Radial pressure gradients

A theoretical analysis of the pressure distribution in a compressible gasket pressed between opposed anvils is quite complicated. Analytical expressions for the pressure distribution require both the theory of elasticity and plasticity [114]. However, the pressure distribution in the gasket has been determined experimentally [115]. Such studies demonstrated that the nature of the pressure distribution, and the magnitude of the radial pressure gradients depended on the diameter of the anvil face and the dimensions of the gasket and the pressure transmitter discs. For a given pair of anvils and with gaskets of fixed
internal diameter, the radial pressure variation depends on the thickness of the gasket. Hence, the pressure distribution in a specific case has to be determined separately by independent experiments.

The pressure distribution in the high pressure cell [Fig.(3.3a)] was studied using the I→II and the III→V transformations of Bi samples (3 x 0.5 x 0.05 mm) placed at different locations across the diameter of the cell as shown in Fig.(3.6). Viewing through a travelling microscope, one of the Bi samples was placed at the centre of the cell, and the distances \( r \), of the other specimens, from the centre of the gasket were noted. The resistances of the Bi samples were monitored by a two-lead arrangement which was adequate to determine the two transformations. These experiments were performed with the gasket thickness as a parameter.

For a given gasket thickness, the cell was assembled in one of the portions of the gasket 0.5 mm thick. The gasket thickness was varied by varying the thickness of the other portion accordingly. The thickness of the pressure transmitter disc was always 10 per cent less than that of the gasket. Systematic studies of the pressure gradient were carried out with talc as the pressure
Fig. (3.6). Arrangement of bismuth samples to map the radial pressure distribution within the cell; $C$ - the centre of the cell, and $r$ - the radial distance of the sample.
transmitter. A few experiments were also made with AgCl and epoxy as pressure transmitters.

The I→II and II→III transformations in each Bi sample were well resolved. The run was terminated after observing the III→V transformation in each sample. The high pressure cell was recovered after unloading, and the distances r of the samples from the centre of the gasket were again measured. It was observed that the radial distances of the samples increased by about 4 per cent, and the diameter of the central hole by about 8 per cent. The central hole of the gasket remained circular without any significant distortion.

Three independent runs were performed for each gasket thickness by placing the Bi samples in nearly the same locations. The values of r from run to run did not vary by more than 10 per cent. The oil pressures corresponding to the start of the I→II and III→V transformations in each Bi sample were obtained using a transducer. The mean values of the oil pressures, \( p_L(r) \), at the Bi transformations were calculated from these data; the standard deviation was 5 per cent.

The differences \( \Delta p(r) = p(r) - p(0) \), where \( p(r) \) is
the sample pressure at \( r \) and \( p(0) \) that at the centre of the cell, were calculated at \( p(0) = 2.55 \) and 7.7 GPa in the following way. It may be noted that \( p_L(0) \) is the oil pressure corresponding to \( p(0) = 2.55 \) or 7.7 GPa, and \( p_L(r) \) are the similar values at \( r \) for \( p(r) = 2.55 \) or 7.7 GPa. Using \( p_L(r) \), the value of \( p(r) \) was determined at \( p_L(0) \). The data obtained with talc as pressure transmitter are shown in Figs.(3.7) and (3.8).

It is seen from Figs.(3.7) and (3.8) that the pressure distribution is axially symmetric. The values of \( \Delta p \) are negative indicating that the pressure at the centre of the cell is maximum and decreases radially. For a given gasket thickness, \( dp/dr \) increases with \( r \), and \( \Delta p \) at a given \( r \) increases with \( p \). These curves indicate that the radial pressure gradients increase with increasing gasket thickness. For 0.8 mm thick gaskets, the pressure distribution is fairly uniform at 2.55 GPa in the region \(-0.8 < r < 0.8 \) mm. In this region, even at 7.7 GPa, \( dp/dr \) is less than 0.1 GPa/mm. This suggests that if the lead distance \( L_1L_2 \) in Fig.(3.3a) is maintained within 1-1.5 mm, the maximum values of radial pressure gradients will be 0.1 GPa mm\(^{-1}\). The 0.9 mm gaskets also have a similar
Fig.(3. 7). Pressure differences at 2.55 GPa as a function of the radial distance; pressure transmitter is talc.
Fig.(3.8). Pressure differences at 7.7 GPa as a function of the radial distance; pressure transmitter is talc.
distribution, as is seen from Figs. (3.7) and (3.8). The choice of 0.8 mm gasket thickness over 0.9 mm was made on the basis of the linearity of the \( p-p_N \) relation. Similar studies with 0.6 and 0.7 mm thick gaskets indicated that for these gaskets the pressure distribution is not well reproduced and strongly depends on the alignment of the press, especially on the parallelism between the platens \( P_1 \) and \( P_2 \). Further, these gaskets had a lower pressure amplification factor; the choice of 0.8 mm thick gaskets over the others is discussed next.

Ideally, the ratio \( x \) of the values of \( p_N \) at the Bi III\( \rightarrow \)V and Bi I\( \rightarrow \)II transformations should be 3.02 for \( p-p_N \) line passing through the origin. If the value of \( x \) is different from 3.02, then either the \( p-p_N \) line drawn through the points \([p_N(2.55), 2.55 \text{ GPa}] \) and \([p_N(7.7), 7.7 \text{ GPa}] \) will not pass through the origin or the points will lie on a curve passing through the origin. Since it is necessary that \( p=0 \) at \( p_N = 0 \), the deviation of \( x \) from 3.02 is taken to indicate the extent of non-linearity of the \( p-p_N \) relation. The value of \( x \) calculated using \( p_N(0) \) was 3.07, 3, 2.8, 2.7 and 2.7 respectively for gasket thicknesses of 0.7, 0.8, 0.9, 1.0 and 1.1 mm. For 0.8 mm thick gaskets, \( x \) is close to
3.02.

The pressure amplification effect in the thicker gaskets used with the opposed anvil apparatus is well known [115]. The pressure amplification factor $p_A = p/p_N$, (obtained using $p_L(0)$) at 2.55 and 7.7 GPa is shown against gasket thickness in Fig.(3.9) for talc, AgCl and epoxy pressure transmitters. It is seen that $p_A$ increases with increasing gasket thickness. It was considered a good compromise to use 0.8 mm thick gaskets in view of the minimum radial pressure gradients and a reasonable value of $p_A$. Further, the increase of $p_A$ with increasing gasket thickness emphasizes the need for a close control on the gasket thickness.

The pressure distributions in the high pressure cells using 0.8 mm and 1.0 mm thick gaskets with AgCl and epoxy pressure transmitters were also determined. The nature of the pressure distribution with AgCl was similar to that with talc. The radial pressure gradients were smaller in magnitude both at 2.55 GPa and at 7.7 GPa. But, the $p-p_N$ relation was highly non-linear and the non-linearity increased with gasket thickness. A linear $p-p_N$ relation is preferred because the arbitrariness involved in drawing a
Fig.(3.9). Variation of the pressure amplification factor with the gasket thickness for different pressure transmitters.
curve through a limited number of data points can introduce uncertainties in the measured specimen pressure.

The nature of the pressure distribution obtained with epoxy pressure transmitter was different from that observed with talc or AgCl in that the pressure at the centre of the cell was minimum, and increased radially. The pressure amplification factors obtained with epoxy pressure transmitter are too low. Based on these considerations talc was preferred as a pressure transmitter in the kinetics studies.

In conclusion, the high pressure resistivity cells using fired pyrophyllite gaskets (12.5 mm o.d., 5 mm i.d., 0.5 and 0.3 mm thick) with talc pressure transmitter discs (5 mm diameter and 0.36 mm thick) and a voltage lead distance of 1.5 mm were found optimum for the kinetics studies.

3.5 High pressure resistivity cell used in kinetics studies

The uncertainties in the determination of sample pressure \( p \) using the mean \( p-p_N \) line were discussed in Section 3.3. In spite of these, the \( p-p_N \) relation was
observed to be very nearly linear in each run, and the ratio $x$ was remarkably constant, the average value of $x$ being $3.00 \pm 0.05$.

The run to run variation in $p$ was taken into account by obtaining the $p-p_N$ relation independently in each run. The sample arrangement shown in Fig.(3.10) was used for this purpose. This was essentially the same as the earlier one shown in Fig.(3.3) with a difference that a Bi sample was placed at right angles to the test specimen in each run. The dimensions of the Bi sample were typically $4 \times 0.5 \times 0.05$ mm, and it was insulated from the sample $S$ by a thin piece of mica ($<0.05$ mm thick). A two-lead arrangement was found adequate to detect the two transformations in Bi. The distance $L_1L_2$ between the leads was typically $1-1.5$ mm. In view of the axial symmetry of the pressure distribution, the distance $LL$ was kept very nearly equal to $L_1L_2$ in all the experiments. For a radial pressure gradient of $0.1$ GPa mm$^{-1}$ (Section 3.4) the pressure at the centre of the specimen differed from that at the leads $L_1$ and $L_2$ by about $0.05$ GPa. In over one hundred experiments made during the study of the kinetics of phase transformations, the ratio $x$ did not differ from $3 \pm 0.05$. The specimen pressure $p$ in these
Fig.(3. 10). The resistivity cell used in the kinetics studies.
experiments was determined by a linear $p-p_N$ relation obtained independently in each run. This method reduced the uncertainty in $p$ significantly.

3.6 Performance of the high pressure resistivity cell

The resistivity cell shown in Fig. (3.10) was used to obtain the resistance-pressure ($R$-$p$) data of Sn, manganin and Ni samples with a view to assessing its performance. The Sn and the Ni samples were prepared from 99.99 per cent pure starting materials. The manganin samples were cut from a wire 0.1 mm in diameter, and used in the as-received condition. The sample pressure and the resistance were determined as described earlier. From these, the $[R(p)/R(0)]-p$ data were obtained up to 10 GPa in each case by continuously increasing the sample pressure at a rate 0.1 GPa min$^{-1}$. The $R(0)$ value was obtained by the extrapolation of the $R(p)-p$ data to zero pressure.

The $R(p)/R(0)$ data of Sn and manganin samples obtained from five independent runs as a function of pressure are shown in Figs. (3.11) and (3.12). The mean $R(p)/R(0)$ for Sn at 2.55 GPa (Bi I$\rightarrow$II) is $0.815 \pm 0.003$ and at 7.7 GPa (Bi III$\rightarrow$V) is $0.643 \pm 0.008$. These values for
Fig. (3. 11). Variation of $R(p)/R(0)$ of tin with pressure; large open circles denote the data obtained in the hydrostatic medium [Ref. 112].
Fig.(3. 12): Variation of $R(p)/R(0)$ of manganin with pressure.
manganin are $1.093 \pm 0.004$ and $1.251 \pm 0.006$. The standard deviation in these values correspond to an uncertainty of 1.5 per cent in the estimated sample pressure as compared to 6 per cent [Fig.(3.4)]. Thus, the uncertainty in the determination of sample pressure is very much reduced by using the cell shown in Fig.(3.10).

It is instructive to compare these data with the data obtained in the hydrostatic medium. The present data for Sn are in good agreement with the data (Fig.3.11) obtained in liquid pressure medium by Eiling and Schilling [112] up to 4 GPa (the two sets of data differing by less than 1.5 per cent), while at 7.7 GPa, the present data are nearly 4 per cent higher. For manganin, the pressure coefficient of resistance obtained from the present data is $0.037 \pm 0.001\ \text{GPa}^{-1}$ whereas the hydrostatic value is $0.023\ \text{GPa}^{-1}$ [116]. The reason for these differences is not clear. However, in the case of manganin, these may arise because of its sensitivity to plastic deformation leading to an increase in the resistivity of the sample. Such an increase was observed in that the resistivity of the manganin wire (0.1 mm in diameter) typically 42.8 micro ohm-cm increased to 72.8 micro ohm-cm when flattened to $0.4 \times 0.05$ mm.
It is seen from Figs. (3.11) and (3.12) that no data points are presented at pressures below 1 GPa. In this region, it was observed that the output voltage across $L_1$ and $L_2$ was unstable and showed an increasing trend with increasing pressure. Presumably this is partly due to the outward movement of the leads $L_1$ and $L_2$ because of the plastic flow of the gasket and partly to plastic deformation of the sample during the initial stages of pressurization. The resistance of the sample was found to exhibit true pressure behaviour only after pressurization to a value between 0.5 and 1 GPa; at higher pressures, the movement of the leads and the plastic deformation effects are reduced.

It may appear that a lead movement in the cell during pressurization may explain the differences in the pressure coefficient of resistance of manganin and $R(p)/R(0)$ values of Sn obtained in the present study, and in the hydrostatic medium. That these differences are not due to the lead movement was confirmed from the resistance-pressure data of Ni.

Two types of Ni samples were used in these experiments. One of the samples was $5 \times 0.5 \times 0.08$ mm cut from a flattened strip, and the other was a wire sample
(0.1 mm diameter) bent in the form of a zig-zag. The leads $L_1$ and $L_2$ contained between them 1.5 mm of the strip sample in one case and nearly 15 mm of wire in the other. For a given change in the lead distance $L_1L_2$, the fractional change in the enclosed length of the strip sample is 10 times that of the wire sample. The resistance-pressure data for both the samples were obtained up to 8 GPa at a constant pressurization rate 0.16 GPa min$^{-1}$. These data shown in Fig.(3.13) are in good agreement with each other.

The pressure coefficient of resistance of Ni obtained from independent runs is $-0.0186 \pm 0.0005$ GPa$^{-1}$ for both the samples, and agrees well with the reported value $-0.0182$ GPa$^{-1}$ [117] obtained in hydrostatic medium. These results indicate that the lead movements, if any, are small and cannot explain the observed differences, in Sn and manganin specimens, between the present and the hydrostatic studies. It must be pointed out that even if the leads are assumed to move slightly during pressurization, the kinetics data obtained under isobaric conditions are not affected.

It was mentioned earlier that the gasket compressed between the anvils undergoes a plastic flow largely during initial loading. This results in a permanent reduction in
Fig. (3. 13). Resistance vs. pressure data of nickel.
its thickness. Beyond a certain load, the flow of the gasket is minimized and further loading results in a nearly elastic compression. Hence, the specimen is likely to undergo a small plastic deformation only in the initial stages of loading. At a given load, the amount of plastic deformation will depend on the yield strength of the specimen. The kinetics of the transformation in some cases may be affected by the plastic deformation of the specimen.

3.7 Pressurization rate

In principle, a pressure induced phase transformation can occur at any pressure $p$ higher than the thermodynamic equilibrium pressure $p_0$. The start pressure of the transformation is determined by the rate of pressurization and the rate of transformation at that pressure. If the rate of pressurization is higher than the rate of transformation, then values of $p$ far removed from $p_0$ can be reached before the start of the transformation. The kinetics data can then be obtained under truly isobaric conditions. Thus, higher pressurization rates extend the range of over-pressures over which the kinetics data can be obtained. The maximum pressurization rate in the present
set-up [Fig. (3.1)] using the motor pump was 0.4 GPa sec\(^{-1}\). This was adequate to reach pressures before any transformation occurred when the transformation time was a few minutes. A much larger rate of loading is required to study the kinetics of faster transformations. This was achieved in the present studies by an experimental arrangement for step-loading the tungsten carbide opposed anvil set-up. Using this set-up, the sample could be pressurized at a rate 10 GPa sec\(^{-1}\) up to 6 GPa.

3.8 Step-loading technique

3.8.1 Step-loading system

The step loading was achieved by an arrangement shown schematically in Fig. (3.14). The high pressure bomb capable of being pressurized to 70 MPa introduced in series with the ram in the existing facility shown in Fig. (3.1) is an additional development. The bomb, the hydraulic ram and the reservoir can be isolated by closing the valves \(V_1\), \(V_2\) and \(V_3\) respectively. In addition, the pump has a built-in non-return valve. The hydraulic ram is first pressurized to a desired initial pressure \(p_i\) by closing \(V_3\) and opening \(V_1\) and \(V_2\); the bomb also gets pressurized simultaneously. The
Fig (3. 14). Schematic of the step-loading arrangement
ram is then isolated by closing $V_2$, and the bomb is pressurized to $p_b (>p_i)$. When $V_2$ is suddenly opened, the ram pressure experiences a jump and finally reaches $p_f$ such that $p_i < p_f < p_b$. The opposed anvil set-up can be operated in the usual manner by closing $V_2$ which isolates the bomb. The magnitude of the ram pressure $p_f$ depends on both $p_b$ and $p_i$ in the manner shown in Fig.(3.15).

3.8.2 Pressure calibration in step-loading

These experiments were performed, using the resistivity cell shown in Fig.(3.10) to examine whether the pressure calibration done under continuous loading is still valid under step-loading. The manganin and Pb specimens were used as the pressure gauges. Each of these was mounted separately with a Bi specimen in the cell. The sample was pressurized at a rate 0.2 GPa min$^{-1}$ until the Bi I$\rightarrow$II transformation was observed. The resistance of the manganin specimen increased (and that of Pb decreased) as shown in Fig.(3.16). The cell was then step-loaded. The resistance-load point marked by the open circle in Fig.(3.16) was obtained. The sample pressure was then increased at 0.2 GPa min$^{-1}$ until the Bi III$\rightarrow$V
Fig. (3. 15). Relation between $P_f$ (the final pressure in the system), $P_b$ (the hydraulic pressure in the bomb), and $P_i$ (the initial hydraulic pressure).
Fig. (3.16). Resistance vs load curves of lead and manganin with intermediate step-loading. A and B denote the resistance-load points at the Bi I→II and Bi III→V transformations. Open circle is the datum point obtained on step-loading.
transformation occurred. It is seen from Fig.(3.16) that the datum point (open circle) after step-loading fell on the resistance-load curve defined by the data obtained during continuous loading. The ratio of the loads at which the Bi transformations occurred in these experiments was $3 \pm 0.05$ in excellent agreement with the value obtained in continuous loading experiments. These experiments suggest that the $p_1$-$p_{\text{r}}$ relation obtained by using the two transformations in Bi is not affected by the intermediate step-loading.

3.8.3 Rise time of the pressure pulse

The rise time of the pressure pulse was estimated from the resistance versus time response of the manganin specimens during a step-loading. The voltage across the leads $L_1$ and $L_2$ (Fig.3.10) was recorded during step-loading on a strip-chart recorder at a chart speed of 1200 mm min$^{-1}$. A typical record is shown in Fig.(3.17a). The rise times in a number of runs made with different values of $p_b$ and $p_1$ were $150 \pm 25$ ms. The changes in the hydraulic pressure of the ram during step-loading were also recorded using the pressure transducer [Fig.(3.17b)]. The shapes and the rise-times of the hydraulic pressure pulse in the ram
Fig. (3.17). Typical records of the changes in (a) the specimen pressure, and (b) the ram pressure during a step-loading.
and the pressure pulse experienced by the manganin specimen placed between the anvils are the same within experimental errors. The traverse time of the recorder pen during these recordings was less than 10 ms, and did not introduce any appreciable error. The maximum height of the pressure pulse was about 2 GPa on the sample pressure scale.

3.8.4 Temperature rise during step loading

The temperature rise $\Delta T(\degree C)$ during step-loading was estimated by placing a chromel-alumel thermocouple on the specimen. A typical trace of the thermocouple output during step-loading is shown in Fig.(3.18). After the pressure step, the temperature decreased rapidly ($\ll 1$ sec) to the ambient. The magnitude of $\Delta T(\degree C)$ was found to depend mainly on the height $\Delta p$(GPa) of the pressure pulse and satisfy the relation $\Delta T = 1.45 \Delta p$. Thus, the temperature rise during step loading is small, and the pressurization by the step-loading method can be considered very nearly isothermal.

3.9 Experiments above room temperature

The anvil system was heated externally using a
Fig. (3. 18). Temperature rise during a step-loading.
heating tape. The maximum temperature reached in these experiments was 358 K. The temperature of the sample was measured with a chromel-alumel thermocouple placed inside the cell. An on-off temperature controller was used to maintain the temperature constant to within ± 0.5 K at a desired value during a kinetics experiment.

The kinetics data of the transformations in Ti and Yb were obtained as a function of pressure and temperature (up to 358 K) using the experimental techniques described so far. The techniques used to obtain the kinetics data of the crystallization process of a-Se are described in the following sections.

3.10 Piston-displacement method

The determination of the compressibility of a solid by the measurement of volume change using the piston displacement observed in a piston-cylinder apparatus is well known [118]. The accuracy in the determination of volume change by this method is 1 part in 10⁴. This technique was used in the present studies for the determination of volume change during the crystallization of bulk a-Se samples under different isobaric-isothermal conditions.
The apparatus is shown schematically in Fig.(3.19). The pressure chamber C was a tungsten carbide cylinder, with 6 per cent cobalt binder, measuring 1.28 cm i.d., 5.08 cm o.d. and 5.08 cm in length, and was used without any binding ring. The sample was retained at the centre of the cylinder by a tungsten carbide element, O, press-fitted in a steel binding ring which formed the central portion of an integral unit consisting of the lever arm, L. The piston (P) was of hardened steel with a bore at the centre for the thermocouple. Both P and O were backed by tungsten carbide blanks B₁ and B₂ respectively. B₁ was press-fitted in a steel binding ring S, surrounding which was an aluminium ring A. The 100 ton press (Fig.3.1) was used to pressurize the assembly. The displacement of P relative to C was determined by measuring the change in distance between L and A. For this, two displacement transducers T (Sangamo make, rated stroke 0.25 cm and a linearity grade ± 0.1% of the total stroke) were located at diametrically opposite points (Fig.3.19). The output of the transducers was 745 mv/mm/10 v excitation.

The sample assembly confined between O and P consisted of the a-Se sample 0.8 cm thick wrapped in lead
Fig. (3.19). Schematic of the experimental set-up for the measurement of volume change by the piston-displacement method.
foil. The flow of the sample past the pistons during pressurization was prevented by using pyrophyllite discs (1.28 cm in diameter and 0.3 cm in thickness), one on either side of the sample. A steel disc 1.28 cm in diameter and 0.2 cm in thickness was placed between the pyrophyllite disc and the piston P.

A chromel-alumel thermocouple contained in a ceramic tube was introduced into the pressure chamber through the bore in P. The sample was heated externally by a furnace wound on the cylinder. The desired temperature was reached at a rate $15^\circ\text{C min}^{-1}$. The temperature during a run was controlled to $\pm 0.5^\circ\text{C}$. For this, the output of a separate thermocouple placed close to the heater wires was fed to an on-off controller which regulated the input power to the heater. The temperature oscillations in the heater were controlled to $\pm 1^\circ\text{C}$ by a periodic manual adjustment of the temperature controller. The temperature gradient in the region of the sample was estimated in blank runs with pyrophyllite by locating the thermocouples at various depths. The temperature at the centre of the sample differed from the temperature at the surface by $0.5^\circ\text{C}$. The stability of the temperature over a 24 hour period during a
run was about 1°C.

The sample pressure \( p \) was determined by measuring the oil pressure and the ratio of the areas of the ram and the piston. There is a loss of pressure inside the pressure chamber which has to be taken into account. This is primarily due to the friction between the movable piston and the wall of the cylinder C. This friction was reduced by smearing the contact surfaces of the piston and the cylinder in each run with MoS\(_2\). Pyrophyllite discs also give rise to a pressure loss depending on the thickness. It is well known that the friction arising from these two causes is symmetrical with respect to the motion of the piston. The contact between the sample material and the cylinder wall is another source of friction and this was reduced by wrapping the sample material in lead foil. The true sample pressure was obtained by correcting the nominal pressure for friction determined by measuring the volume change of the Pb sample with increasing and decreasing pressures. Typically, the values of friction (Fig. 3.20) were in the range 0.07 GPa at 0.35 GPa and 0.08 GPa at 0.8 GPa.

The piston displacements were obtained from the output voltages of the transducers recorded continuously.
Fig. (3. 20). Displacements of the piston under both increasing and decreasing oil pressures; sample - lead. Curves (a) and (b) were obtained respectively under increasing and decreasing loads; (c) is the mean curve.
during the run. The values of the displacements recorded by the transducers did not differ by more than 0.05 mm. The mean of these two readings was taken to obtain the piston displacement at any instant. The piston displacement was measured to a precision of 0.00013 cm. The typical value of the total piston displacement for complete crystallization was in the range 0.7 - 1.0 mm.

A larger sample size (1 cm$^3$) such as the one used in the present studies, while giving a higher sensitivity in the volume change measurements, leads to a pressure drop as the transformation progresses. The pressure drop will be large enough to affect the transformation rate and consequently, isobaric conditions will not prevail. This problem was solved by using a bladder-accumulator in place of the high pressure bomb shown in Fig.(3.14).

The bladder, pre-charged to an appropriate gas pressure (20 per cent of the hydraulic pressure), was compressed to the required pressure by keeping $V_1$ open, and $V_2$ closed and pumping oil. After the desired pressure in the accumulator was reached, $V_1$ was closed. The opposed anvil apparatus was then operated by opening $V_2$. The hydraulic pressure of the experiment was set at the desired value when
required by opening $V_1$. The oil pressure increased to the desired value in a few seconds. The accumulator connected in series with the ram made up for the difference in fluid volume caused by the movement of the piston and maintained the oil pressure constant within detectable limits during the run. It also took care of any change in the fluid volume caused by temperature changes during heating or cooling of the specimen.

3.11 Microscopic observation of the partially crystallized samples

The data obtained by the piston—displacement technique refer to the kinetics of the overall process of crystallization of amorphous selenium under different isobaric-isothermal conditions. The crystallization was observed to proceed through the spherulitic growth. The microscopic examination of the spherulites in partially crystallized samples obtained under these conditions appeared promising to reveal the details of the various processes underlying the crystallization. Hence, the crystallization of Se specimens was allowed to progress by annealing them for various time intervals under
pre-determined conditions of pressure and temperature and then the specimens were quenched to ambient conditions. The isobaric-isothermal conditions were maintained during a run as explained in the preceding section. The only difference was that the sample space consisted of a teflon cup containing pieces of amorphous selenium (4 x 3 x 3 mm) immersed in silicone oil. No measurements of crystallization were made during an annealing experiment. After the annealing, the partially crystallized samples were quickly recovered, ground to remove the surface layers and prepared for microscopic examination by routine metallographic techniques. The Neophot 2 microscope was used to observe the polished surface of the specimen under polarised light, and the randomly selected regions of the sample were photographed. The diameters of the circular sections of the spherulites were measured from these photographs using a Hewlett-Packard digitizer.

3.12 Calculation of the transformed fraction

The study of the kinetics of phase transformations requires information on the fraction transformed ($\zeta$) as a function of time ($t$). The methods used to calculate $\zeta$ from
the measurements of change in resistance and volume associated with the transformation are described in this section.

3.12.1 Resistometric method

The method is explained with reference to the resistance-pressure data, typical of Ti specimen, shown in Fig.(3.21). As the pressure is increased, the resistance of $\alpha$-Ti decreases, and at a sufficiently high over-pressure, the transformation to $\omega$-phase starts. The resistance of the specimen becomes time-dependent, and is recorded as a function of time. In general, the $\alpha$ phase is taken to denote the low pressure phase (l) and $\omega$ phase to denote the high pressure phase (h) in a typical pressure-induced transformation. The specimen is fully in the low pressure phase before the start of the transformation and fully in the high pressure phase after the completion of the transformation. During the transformation, the specimen can be considered as an intimate random mixture m of both the phases l and h and its resistance is denoted by $R_m(t)$. The quantities $r = R_h - R_l$ and $\Delta r(t) = R_m(t) - R_l$ denote respectively the total and the instantaneous resistance
Fig.(3. 21). Typical resistance vs. pressure data of titanium undergoing $\alpha \rightarrow \omega$ transformation.
changes at and during the transformation.

The volume fraction is defined in the following way. At any instant \( t \), the volume \( V \) of the specimen undergoing a phase transformation can be written as

\[
V = v_l + v_h
\]  
(3.1)

where \( v_l \) and \( v_h \) refer to the instantaneous volumes of the low and the high pressure phases. Then the volume fraction \( \zeta \) is \( v_h/V \) and can be calculated if an expression, relating it to \( R_m(t), R_l \) and \( R_h \), is known.

The simplest relation can be derived by assuming that the resistivity \( \rho_m \) of the mixture of the two phases is given by

\[
\rho_m(t) = (1 - \zeta) \rho_l + \zeta \rho_h
\]  
(3.2)

Replacing the resistivities by the respective specimen resistances, Eq.(3.2) can be solved to obtain

\[
\zeta = \frac{\Delta r(t)}{r}
\]  
(3.3)

This expression will be correct if the phases were arranged in alternate layers perpendicular to the direction of current. In this model, the current cannot avoid the regions of high resistance as it would if the regions were arranged
at random. Therefore, Eq.(3.2) gives an upper limit for $\rho_m(t)$. As an alternative, the electrical conductivities can be assumed to be additive. This gives

$$\sigma_m(t) = (1-\zeta) \sigma_1 + \zeta \sigma_h \quad (3.4)$$

Assuming that the conductivities are proportional to the inverse of the respective specimen resistances, Eq.(3.4) can be solved to obtain

$$\zeta = \frac{\Delta r(t)}{1 + \Delta r/R_1} \quad (3.5)$$

Equation (3.4) corresponds to a model in which the phases are arranged in layers parallel to the direction of current flow and gives an upper limit for $\sigma_m(t)$. Obviously the actual situation lies between these two extreme cases.

The electrical conductivity $\sigma_m(t)$ of a specimen containing a random mixture of two phases in terms of the electrical conductivities of the component phases was derived by Landauer [119]. The equation for $\sigma_m(t)$ is

$$\frac{x_1(\sigma_1 - \sigma_m)}{\sigma_1 + 2\sigma_m} + \frac{x_2(\sigma_2 - \sigma_m)}{\sigma_2 + 2\sigma_m} = 0 \quad (3.6)$$
where \( x_1 \) and \( x_2 \) are the volume fractions of the phases 1 and 2. Taking phases 1 and 2 to designate respectively the low and the high pressure phases and replacing \( x_2 \) by \( \zeta \), \( x_1 \) by \( (1-\zeta) \) and the various conductivities by the inverse of the respective specimen resistances one gets

\[
\left[ 1 - \zeta \right] \left( \frac{1}{R_1} - \frac{1}{R_m} \right) \zeta \left( \frac{1}{R_h} - \frac{1}{R_m} \right) = 0 \quad (3.7)
\]

\[
\left( \frac{1}{R_1} + 2/R_m \right) \left( \frac{1}{R_h} + 2/R_m \right)
\]

Equation (3.7) can be simplified to give the following result,

\[
\zeta = \frac{\Delta r(t)}{r} \times \frac{1 + (2r/3R_1) + (\Delta r(t)/3R_1)}{1 + \Delta r(t)/R_1} \quad (3.8)
\]

It is seen from Eq(3.8) that at the beginning of the transformation i.e. when \( t=0, \Delta r(0)= 0 \) and \( \zeta = 0 \). At the end of the transformation i.e. when \( \Delta r=r \), Eq.(3.8) gives \( \zeta = 1 \). The \( \zeta \)-t data of the transformations in Ti and Yb are calculated from the experimentally measured R-t data using Eq.(3.8).

The variations in \( \zeta \) resulting from using different models of the effective electrical conductivity of a two-phase mixture were also examined. These results are discussed in appendix 1. It was observed that the values of \( \zeta \) calculated from the various models did not differ widely.
for the $\alpha\rightarrow\omega$ transformation in Ti. But the differences were rather large for the fcc$\rightarrow$bcc transformation in Yb. The resistance increases by 30 per cent in going from $\alpha$- to $\omega$-Ti and decreases by 90 per cent for the fcc$\rightarrow$ bcc-Yb transformation. The $\zeta$ values obtained from different conductivity models differ appreciably when the magnitude of the resistance change at the transformation increases.

It must be pointed out that Eq.(3.8) was derived from Eq.(3.6) by replacing the conductivity terms by the inverse of the respective specimen resistances. This amounts to neglecting the density change associated with the transformations. The increase (decrease) in density during a pressure (temperature) induced transformation will result in contraction (expansion) in the specimen dimensions. Assuming that the bulk specimen is elastically isotropic and that the leads $L_1$ and $L_2$ move along with the specimen as the transformation progresses, the effect of the density change on $\zeta$ was estimated. These results are discussed in appendix 2. The density change corrections were not more than a few per cent for most of the solid-solid transformations encountered in practice and negligible for the transformations in Ti and Yb.
3.12.2 Volumetric method

The determination of the crystallized fraction by the volumetric method is explained using Fig.(3.22) which shows schematically the compression behaviour of a typical solid undergoing a first order phase transformation. Let $V_a$, $V_c$ and $V_m(t)$ denote the volumes of the specimen before, after and during crystallization. Similarly $D$ and $M$ denote respectively the density and mass of the specimen. The suffixes $a$ and $c$ refer to the amorphous and the crystalline phases and the suffix $m$ to the intermediate phase which is a mixture of both $a$ and $c$. In the intermediate phase, the instantaneous masses ($m_a$, $m_c$) and volumes ($v_a$, $v_c$) are additive and a separate consideration of these leads respectively to volume and mass fractions. In a two-phase system, the additivity of amorphous and crystalline volumes gives

$$V_m(t) = v_a(t) + v_c(t) \quad (3.9)$$

Eq.(3.9) can be re-written as

$$\frac{1}{D_m(t)} = \frac{1}{D_a} \frac{m_a}{M} + \frac{1}{D_c} \frac{m_c}{M} \quad (3.10)$$

and this leads to
Fig.(3.22). Schematic compression behaviour of a solid undergoing a first order phase transformation.
\[ \zeta_M(t) = \frac{D_m(t) - D_a}{D_m(t)} \times \frac{D_c}{D_c - D_a} \]  

(3.11)

where \( \zeta_M = m_c/M \), the crystallized mass fraction, and \( m_a/M = 1 - \zeta_M \). In terms of specific volumes, Eq.(3.10) gives \( \zeta_M \) as

\[ \zeta_M(t) = \frac{\overline{V}_a - \overline{V}_m(t)}{\overline{V}_a - \overline{V}_c} \]  

(3.12)

Thus, the crystallized mass fraction at any instant \( t \) is the ratio of the instantaneous volume change \( \Delta V(t) \) to the total volume change \( \Delta V \) at the crystallization. It may be noted that in the piston-displacement technique both \( \Delta V(t) \) and \( \Delta V \) are directly measurable quantities, and the calculation of \( \zeta_M(t) \) does not require the absolute magnitudes of \( \overline{V}_a \), \( \overline{V}_c \) and \( \overline{V}_m(t) \). In terms of the piston-displacements, Eq.(3.12) reduces to

\[ \zeta_M(t) = \frac{\text{instantaneous piston displacement}}{\text{total piston displacement}} \]  

(3.13)

The Eq.(3.13) was used to calculate \( \zeta_M(t) \) from the piston-displacements obtained during the crystallization of a-Se under different isobaric-isothermal conditions.

Alternatively, if the additivity of masses is
considered, then

\[ M = m_a(t) + m_c(t) \quad (3.14) \]

This can be rewritten as

\[ D_m(t) V_m(t) = D_a V_a(t) + D_c V_c(t) \quad (3.15) \]

and

\[ D_m(t) = D_a (1 - \zeta_v(t)) + D_c \zeta_v(t) \quad (3.16) \]

where \( \zeta_v(t) = V_c(t)/V_m(t) \) is the crystallized volume fraction. Equation (3.16) simplifies to

\[ \zeta_v(t) = \frac{D_m(t) - D_a}{D_a - D_c} \quad (3.17) \]

It is seen from Eqs. (3.11) and (3.17) that the mass and the volume fractions are related by

\[ \zeta_M(t) = \frac{D_c}{D_m(t)} \zeta_v(t) \quad (3.18) \]

The densities of the amorphous and the crystalline phases of Se at atmospheric pressure are respectively 4.278 and 4.8 g cm\(^{-3}\). Using these values in Eq. (3.18), it turns out that in the initial stages of crystallization, \( \zeta_M(t) \) and \( \zeta_v(t) \) differ by 12 per cent, and the difference reduces as the crystallization progresses.