High pressure investigations on amorphous selenium

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Abstract. We report the diamond anvil cell (DAC) high pressure powder X-ray diffraction studies on amorphous selenium (a-Se) under truly hydrostatic pressure condition up to 20 GPa. Amorphous selenium exhibits a sharp and irreversible transition to a hexagonal structure at 10.6 ± 0.1 GPa. It is also known that metallization occurs in a-Se around this pressure. Some plausible arguments are provided to suggest that the amorphous to crystalline transition may be driven by metallization.

1. Introduction

Recently there has been a lot of interest in the study of the structural order exhibited by covalently bonded chalcogenide glasses [1–4]. The investigations have clearly revealed that there remains a lot to be studied about the structural order in these glasses. It is difficult to get a complete picture from any single experimental method. Techniques like Raman spectroscopy, EXAFS, XRD and DSC provide useful information on these systems.

Selenium belongs to the chalcogen group and is one of the elemental systems to form bulk glassy state. Its polymer like properties in the liquid state makes crystallization very difficult. Crystalline selenium has basically two solid modifications: hexagonal and monoclinic [5]. Whereas hexagonal selenium (h-Se) consists of chains of selenium atoms, monoclinic (m-Se) is made up of rings of Se_6 molecular units. At ambient conditions, h-Se is the stable form. Recent studies by Andonov [6] on the structure of amorphous selenium (a-Se) have conclusively pointed out that it is made up of entangled helical chains. Further, liquid selenium (l-Se) exhibits similar structure as that of a-Se at temperatures near the melting point [7–9]. Recently exhaustive studies on nucleation, growth kinetics and modes of crystallization of l-Se were reported by Ryschenkow and Faivre [10] and Bisault et al [11].

Considerable amount of literature exists on high pressure studies on h-Se [12–17]. In the most recent work of Tanaka [18] in 1990, the structure of a-Se is investigated up to 14·0 GPa. He observed a phase transition from amorphous phase to hexagonal phase in the pressure range of 9·7 to 14·0 GPa. The precise transition pressure is not reported in this work. The pressure induced changes in the X-ray diffraction pattern

are accounted for using a microcrystalline model, assuming large contraction between interchain distances. It is important to note here that in Tanaka's [18] work, the hydrostatic pressure limit was only up to 10·4 GPa. Our primary intention was to perform experiments with hydrostatic pressure environment, determine the precise transition pressure and try to throw some light on the nature of the transition.

The other motivation stems from the fact that the high pressure crystalline structure of selenium is yet to be determined unambiguously. It is not yet clear whether the 1 atm h-Se (stable form) is identical to the high pressure h-Se.

A brief preliminary report on high pressure X-ray diffraction on a-Se is published elsewhere [19]. In this paper we report in detail our investigations on the pressure induced structural changes in a-Se.

2. Experimental

High purity selenium (99·999%) obtained from M/s Hoboken, Belgium, was used in this study. The spherical lumps of selenium were powdered and characterized by X-ray diffraction. The X-ray diffractogram of the starting material is shown in figure 1. It shows that the material consists of a mixture of amorphous and hexagonal phases of selenium. The powder was taken in a silica tube, evacuated to 10^{-6} Torr and finally sealed with inert gas pressure of ~ 0.06 MPa. The material was then melted and quenched from 523 K to liquid nitrogen temperature. The X-ray diffraction pattern of a-Se thus obtained is shown in figure 2. It shows a broad halo peak around $2\theta = 27°$ with Cuk_α radiation. The frozen bulk a-Se was then powdered to the required particle size for high pressure experiments with the diamond anvil cell. The high pressure X-ray diffraction technique is described in detail elsewhere [20]. The methanol–ethanol–distilled water mixture in the ratio 16:3:1 was used as the pressure transmitting medium. The generated pressure was determined using the ruby fluorescence wavelength shift technique. It was noticed that the pressure environment remained hydrostatic up to 19 GPa. This was evident from clearly resolvable ruby R_1 and R_2 peaks shown in figure 3.

The energy dispersive X-ray diffraction experiments were performed using the polychromatic X-ray from a RIGAKU 18 kW rotating anode X-ray generator with molybdenum target. The diffracted beam was detected using a high purity planar
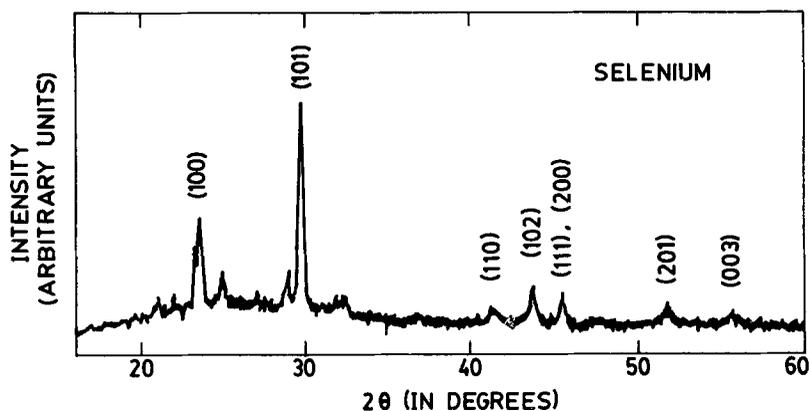

Figure 1. X-ray diffraction pattern of the starting material showing an amorphous background superimposed with sharp peaks indexed to hexagonal structure.
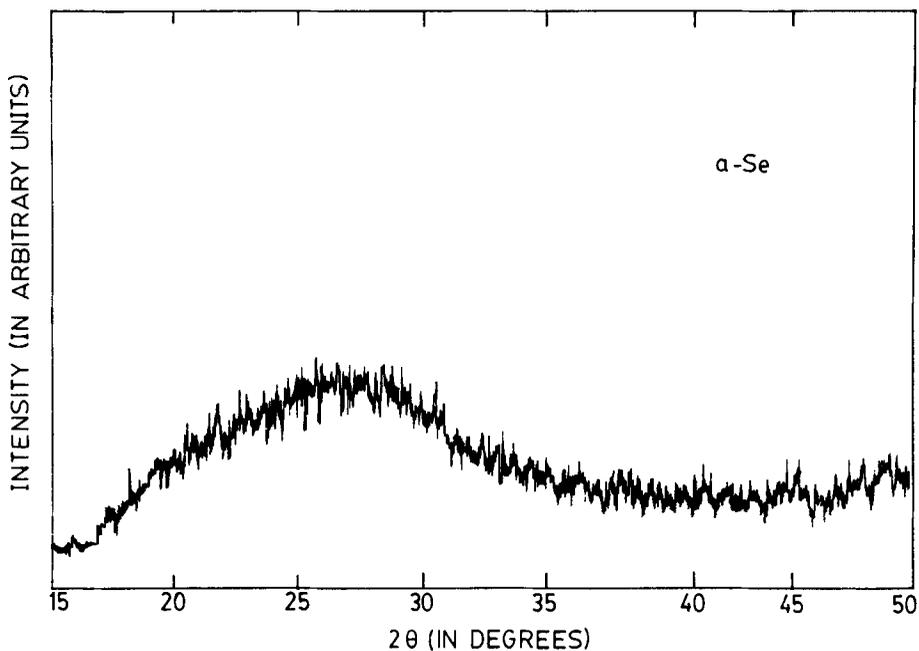
Figure 2. X-ray diffraction pattern of quenched selenium showing clearly the amorphous nature. The pattern peaks around $2\theta = 27°$.
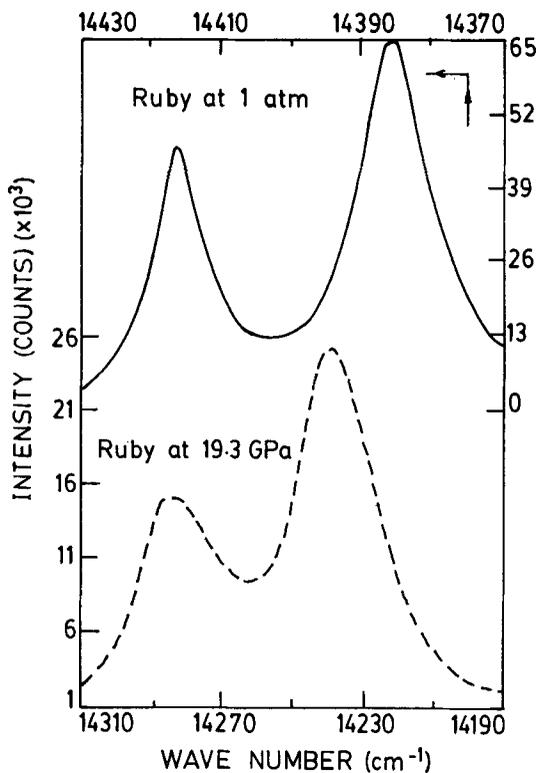

Figure 3. The ruby spectrum showing the R_1 and R_2 peaks clearly resolvable at $19 \cdot 0\,GPa$, indicating the truly hydrostatic pressure environment in the DAC.

germanium detector. The energy resolution of the detector is 500 eV at 60 keV. The data aquisition and processing was done using a PC-based MCA system. The lattice spacing resolution for our system was less than 0·01 Å.

3. Results

The energy dispersive X-ray diffraction data for a-Se are shown in figure 4 for selected pressures. The spectra were taken at an angle of $2\theta = 11°$, an optimum value for the signal-to-noise ratio and the resolution. As is evident from figure 4, a-Se shows a broad halo in the range of 1·459–2·529 Å^{-1} and this feature is retained up to 10·4 GPa. This amorphous feature agrees well with the earlier result [6]. At 10·6 GPa a sharp transition is observed in that the halo is split into three well defined peaks. The sharp transition at 10·6 GPa may be due to the better hydrostatic pressure environment around the sample. However, it is known that the a-h transition start pressure depends on thermal history of the sample. This structure continues to be stable up to 17·0 GPa. At 17·5 GPa another allotropic modification occurs.

The crystalline phase at 10·6 GPa is identified to be hexagonal with atomic volume $V = 20·76$ Å^3, $a = 3·73$ Å and $c = 5·17$ Å. Significantly these parameters are close to that of stable hexagonal phase compressed to 10 GPa. Thus, the a-h transition is accompanied by no appreciable change in the atomic volume as can be noted from
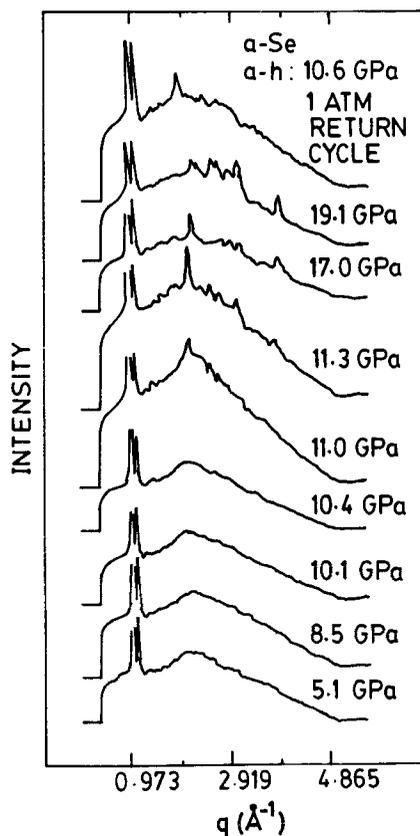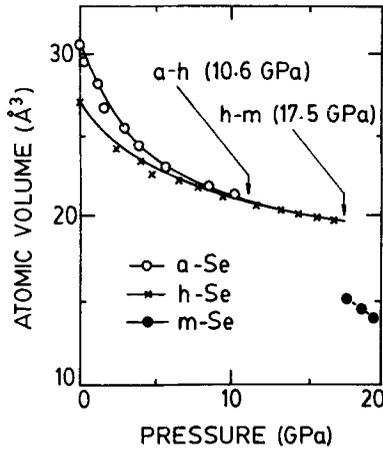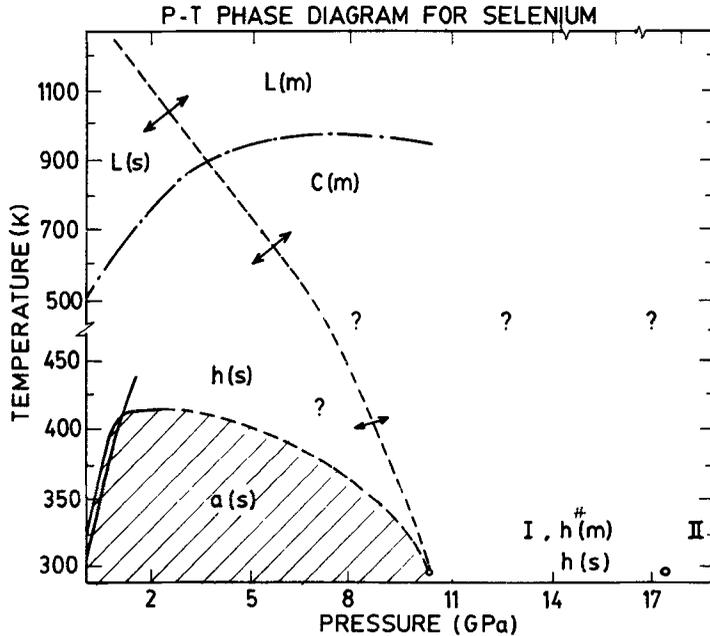

Figure 4. EDXD spectra of a-Se at selected pressures taken at $2\theta = 11°$. Sharp peaks at 1·459 and 2·529 Å^{-1} correspond to k_{α_1} and k_{α_2} fluorescences of Se.

Figure 5. Pressure dependence of atomic volume in a-Se and h-Se. a-h transition at 10·6 GPa is accompanied by almost negligible volume change. h-m transition occurs at 17·5 GPa.

Figure 6. P–T phase diagram for Se. Here, L-liquid, C-crystalline, m-metallic, a-amorphous, s-semiconducting. The dot and dash line is the liquidus, indicating T_m, the melting temperature. The thick line indicates the T_g (glass transition temperature) variation with pressure. $\langle - - \rangle$ indicates s-m transition across a hypothetical curve. Open circles gives our data points. I is hexagonal phase, and II the monoclinic.

figure 5. Structure of the allotrope above 17·5 GPa is monoclinic. At 19·3 GPa, the cell parameters for this structure are obtained to be $V = 15·0\,\text{Å}^3$, $a = 3·27\,\text{Å}$, $b = 4·14\,\text{Å}$, $c = 3·35\,\text{Å}$ and $\beta = 97°$. Further, whereas hexagonal to monoclinic phase transition is observed to be reversible, the a-h transition is irreversible in nature.

In figure 6 the pressure–temperature diagram of selenium reported by Tanaka [18]

GENERALISED PHASE DIAGRAM
FOR COVALENT INSULATORS
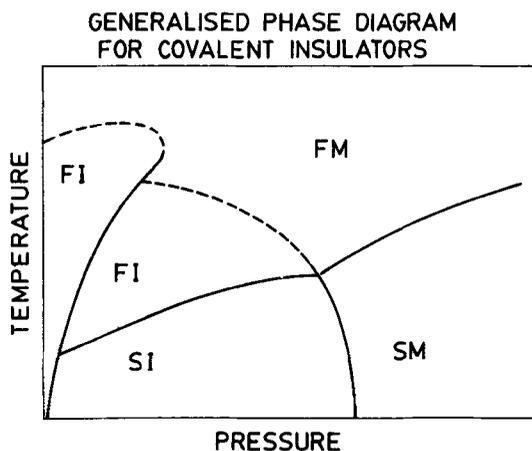
Figure 7. Schematic phase diagram showing insulator to metal transitions in covalent insulators by Young [21]. Here, F-fluid, M-metal and S-solid.

in 1990 is reproduced with additional features observed by us. It is interesting to observe that if h-Se (h(s)) is pressurized, it becomes at best a semiconducting crystalline solid at 10·6 GPa, whereas a-Se (a(s)), at 10·6 GPa becomes a crystalline metallic solid (h(m)). The stable h-Se undergoes metallization at 17·5 GPa which is accompanied by h-m transition. It, therefore, transpires that insulator to metal transition pressure in selenium is reduced from 17·5 GPa to 10·6 GPa, if the starting structure is glassy rather than hexagonal. Figure 6 also shows the pressure dependence of the melting temperature T_m and the glass transition temperature T_g. The crystallization induced by the hydrostatic compression occurs at 10·6 GPa at room temperature which is below the glass transition temperature. The probable direction in which metallization curve may proceed at higher temperatures is shown as dotted lines. It is illuminating to compare figure 6 with a generalized P–T diagram proposed by Young [21] for covalent insulators, shown in figure 7. High temperature–high pressure X-ray diffraction experiments may be able to throw more light on other regions in the diagram.

4. Discussion

We examine here two important aspects of the phase transition: (i) the structure of the high pressure phases of selenium: phase I appearing at 10·6 GPa and phase II at 17·5 GPa, and (ii) the nature of the phase transition at 10·6 GPa.

The structure of phase I at 10·6 GPa was found to be hexagonal. Here it is worthwhile to note that Se exhibits two types of hexagonal modifications [22]: one generally reported consists of Se_8 units and the other Se_6 units. In our investigations, we find that the h-Se obtained from a-Se at 10·6 GPa seems to be the former type, since its lattice parameters agree to a good extent with the usual hexagonal phase compressed to 10·6 GPa. The parameters of phase II at 17·5 GPa was found to fit with that of a monoclinic structure. The nature of this phase transition is discussed in detail by other workers [13] and their argument is briefly reproduced in the reference.

Turning our attention now to the crystallization of a-Se, observed at 10·6 GPa, we refer to Tanaka [18]. In his report, the mechanism of the transition is explained using two routes. The first is the thermodynamic transition model from one equilibrium
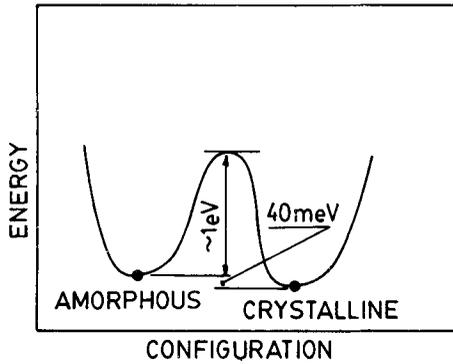
Figure 8. Configuration vs energy for h-Se and a-Se at 1 atm.

phase to another equilibrium phase [23]. The energy needed for the transition is supplied by the hydrostatic compression. The second treatment refers to crystal growth aspects which occurs in the non-equilibrium states such as in the supercooled liquids. The crystallization of the a-Se cannot be understood in the light of the thermodynamic phase transition model. The reason is as follows. The free energy difference between a-Se and h-Se at 10·6 GPa is

$$\Delta G|^{a\text{-}h}_{10\cdot6\,\text{GPa}} \sim \int_0^{10\cdot6\,\text{GPa}} \{V^a(P) - V^h(P)\}\,dP \sim 0\cdot1\,\text{eV}.$$

As the configurational energy difference between a-Se and h-Se (figure 8) is $\sim 1\,\text{eV}$ [24], $\Delta G|^{a\text{-}h}_{P=10\cdot6\,\text{GPa}}$ is not adequate to drive the a-h transition.

Tanaka [18] gives the second argument as follows. The interchain distances dramatically contract and fluctuate spacially reflecting random structures, and then, at some local regions, where the interchain distance is shorter than the average, the critical condition $[R_P]/[R_{1\,\text{atm}}] = 0\cdot86$ may be fulfilled. Here, R is the first nearest interchain distance and P stands for pressure. A bond interchange occurs, which is responsible for crystal nucleation and as a consequence, the peripheral parts successively get converted into the crystalline phase. In this crystal growth process, no macroscopic atomic diffusion is needed, since the densities of the a and h phases are nearly the same. It is also worth recollecting here that this transition is also accompanied by metallization. Tanaka [18], ends his discussion by stating that for any quantitative analysis a deeper insight into the degree of the interchain distance fluctuation as a function of pressure is needed.

Not satiated by the arguments given above, we present in the following, the nature of the crystallization of a-Se leading to a new suggestion for explaining the transition. Minomura [25] in 1985 reported that a-Se undergoes metallization at $\sim 10\,\text{GPa}$. The conductivity obeys the relation $\sigma = C\exp(-E/kT)$. The constant C is of the order of 10^2 to 10^4 (ohm-cm)$^{-1}$. a-Se shows an exponential decrease in the resistivity over several orders of magnitude as shown in figure 9 [25]. From the figure it is clearly seen that the resistivity of h-Se is lower than that of a-Se until the cross-over is around $10\,\text{GPa}$. The reasons for higher resistivity in a-Se can be attributed to topological disorder. It is evident from the figure that up to $\sim 10\,\text{GPa}$, it is the topological disorder that dominates the effect in a-Se. Suddenly at $\sim 10\,\text{GPa}$, the survival of disorder is at peril. As to what causes this transition is the question, the answer to which we are trying to probe.
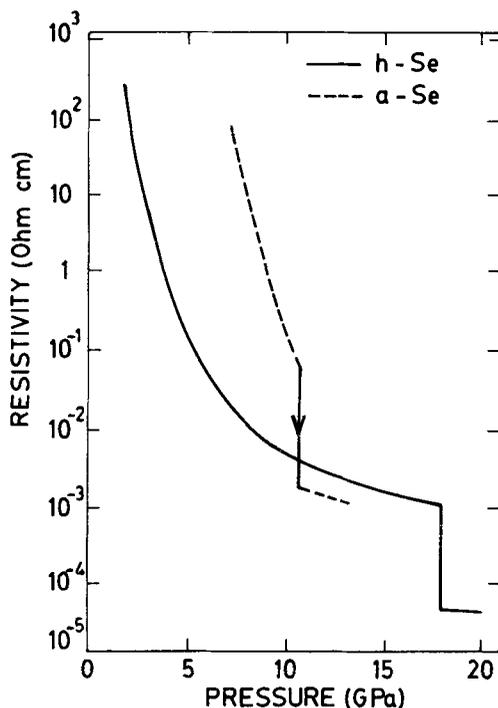
Figure 9. Variation of resistivity with pressure for amorphous and crystalline selenium.

If we take another look at the figure 9 it is seen that in h-Se, resistivity decreases with pressure, but never so low as to become a metal, until a pressure as high as 17·5 GPa is applied where it drops down quickly to metallic values. Here it is interesting to investigate as to why a-Se metallizes before h-Se as a function of pressure. The structure of a-Se is described as consisting of majority of entangled helical chains of Se atoms. Structure of h-Se consisting of chains of Se atoms is shown in figure 10. In a-Se there is a random distribution in the interchain distance R. It is also well known that this randomness in structure gives rise to diffuse band boundaries. The valence and the conduction bands are now closer than the ones in h-Se. As the pressure is increased, the probability of some of these chains coming very close and closing of the energy gap increases rapidly. At 10·6 GPa, a nucleation of such an event occurs followed by a cascade. This raises the question of stability of such a material. It is now well known that the possibility of having a bulk, amorphous single constituent metallic solid is extremely difficult.

In the light of the above arguments, we suggest an idea that it could be the metallization which drives the crystallization of a-Se under pressure. This suggestion gains support from some earlier investigations and results. Cahn [26] has studied the formation and stability of metallic glasses and in his report the required cooling rates for the formation of amorphous monoatomic metals are given in the range 10^{12}–10^{13} Ks^{-1}. Studies by Cargill [27] and Chen and Jackson [28] report similar results. Also reports of bulk elemental amorphization are nonexistent in the literature. In a recent review by Yonezawa [29] it is mentioned that metals with atoms having isotropic environment are difficult glass formers. Even in amorphous state, the system of isotropic atoms has finite probability of relaxing towards crystalline structures. If
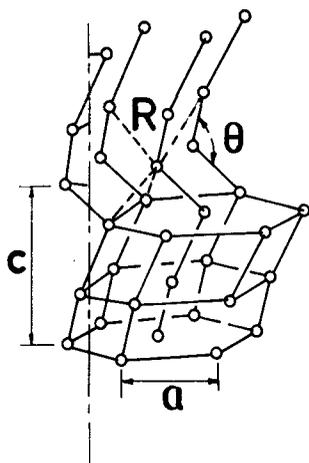
Figure 10. Structure of hexagonal selenium after transition from amorphous state.

we look at the Se atom in the a-Se state, it is presented with almost an isotropic environment because of the similar magnitudes the inter and intra chain bond strengths. Such a situation does not permit the material to be in the amorphous state any more and drives it into crystalline state resulting with a hexagonal structure. However, an in situ experimental evidence, possibly optical reflectivity along with X-ray diffraction studies with the diamond anvil cell, is needed to confirm the above proposal.

5. Summary

The report is summarized into the following important points.

1. Amorphous selenium was investigated under truly hydrostatic pressure up to 19 GPa.
2. The amorphous phase (a-Se) transforms into the hexagonal crystalline phase at 10·6 GPa irreversibly. Further, at 17·5 GPa it goes over to monoclinic phase reversibly.
3. Arguments based on the behaviour of the electrical resistivity and that of the structure is presented to suggest that metallization could be precursor to the a-h transition in a-Se.
4. In the existing phase diagram of Se certain new features, drawn from the present investigation, have been incorporated.

Acknowledgements

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