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Pressure-induced electronic and structural transformations in bulk $GeSe_2$ glass

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Abstract. The pressure dependence of the electrical resistivity of bulk $GeSe_2$ glass shows a semiconductor-to-metal transition at 7 GPa pressure. The high pressure phase is examined using the x-ray diffractometer and is found to be crystalline, with a face-centred cubic structure having $a = 4{\cdot}06$ Å. The electrical conductivity has also been studied as a function of temperature at various pressures.

Keywords. High pressure effects on solids; semiconductor-to-metal transition; chalcogenide glasses; amorphous to crystalline transformations.

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1. Introduction

Amorphous chalcogenides have attracted considerable attention because of their interesting electrical and optical properties, which are useful for device applications. In amorphous semiconductors the pressure-induced semiconductor-to-metal transition is one of the most interesting phenomena (Shimomura *et al* 1974; Minomura 1978, 1980, 1982; Sakai and Fritzsche 1977; Parthasarathy *et al* 1984a, b; Bhatia *et al* 1984). The primary effect of pressure is to decrease the interatomic distances, which give rise to changes in the electronic structure and hence sometimes to electronic transitions. Earlier studies on the effect of pressure on glasses show that the amorphous chalcogenides become metallic under pressure with a continuous decrease in the electrical resistivity and the energy gap (Sakai and Fritzsche 1977; Parthasarathy *et al* 1984a, b; Bhatia *et al* 1984). On the other hand, the tetrahedrally bonded materials make a discontinuous transition from a semiconductor to a metal with a sudden jump in electrical resistivity, associated with the changes in structure to high coordination (Shimomura *et al* 1974; Minomura 1978).

The sample $GeSe_2$ has been chosen because the studies of the composition dependence of the band edge in Ge_xSe_{1-x} alloys had shown rapid variations with a narrow peak at $x = 1/3$ (Nemanich *et al* 1978). Moreover for $GeSe_2$ the molecular structure has been explained in terms of molecular clusters which lead to a new phenomenon called 'quasi crystallization' (Griffiths *et al* 1982). For understanding the local molecular structure and the nature of bonding, we have studied the effect of pressure on the electrical resistivity of bulk $GeSe_2$ glass.

2. Experiments

High pressure electrical resistivity was measured using a Bridgman anvil system made of tungsten carbide anvils. The anvils were calibrated at room temperature as well as at liquid nitrogen temperature (Parthasarathy and Gopal 1984). The sample was embedded in a steatite pressure transmitting medium and surrounded by a heat-treated pyrophillite gasket of thickness 0·15 mm. The cell was pressurized by a hydraulic press to the desired extent. Sodium chloride was used as the pressure transmitting medium and the pressure quenched samples were recovered by dissolving the pressure transmitting medium in double distilled water.

$GeSe_2$ glass was prepared from appropriate amounts of germanium (99·999 % pure) and selenium (99·999 % pure) in a evacuated (10^{-6} torr) quartz ampoule (6 mm i.d.). The mixture was heated at 1200 K for 5 hr with constant rotation of the ampoule (10 rpm) inside a rotary furnace to ensure complete mixing. The molten alloy was then quenched directly from the furnace into ice-water mixture. The glassy nature was confirmed by x-ray diffraction and electron microscopic studies.

To measure the electrical resistivity the conventional four-probe method was employed. At room temperature and atmospheric pressure the resistivity of the sample was measured by the Van der Pauw (1958) technique. The decrease in the dimensions of the sample with pressure was neglected, because its effect on the electrical resistivity is very small when compared to the total change in the resistivity. The correction requires the high pressure compressibility data, which are not known.

A Keithley constant current source (model No. 225), a Keithley digital multimeter (model No. 177) and a Keithley electrometer (model No. 616) were used as the measuring units. A copper-constantan thermocouple was used to measure the temperature. The error involved in the pressure measurements is $\pm 0{\cdot}1$ GPa in the range up to 5 GPa and $\pm 0{\cdot}2$ GPa up to 8 GPa. The error involved in the temperature measurements is $\pm 0{\cdot}1$ K.

3. Results and discussion

Figure 1 shows the variation of the electrical resistivity as a function of pressure. At room temperature and at atmospheric pressure the resistivity value is approximately $3{\cdot}04 \times 10^{11}$ ohm-cm. The resistivity increases with pressure up to 2 GPa by roughly two orders of magnitude. Usually the pressure coefficient of resistivity for tetrahedrally bonded materials is positive (Minomura 1982). The earlier experimental studies on the structure of Ge_xSe_{1-x} show that the molecular structure of virgin, melt-quenched $GeSe_2$ glass is much more ordered than would be expected from a continuous random network model. Phillips (1979) described chalcogenide glass alloys by a model of small chemically ordered cluster embedded in a continuous network (Lucovsky *et al* 1974, 1977a, b; Lucovsky 1979). The predominant clusters are $(Se)_n$ chains $Ge(Se_{1/2})_4$ corner sharing tetrahedra and $Ge_2(Ge_{1/2})_6$ ethane-like structural units, which dominate Ge_xSe_{1-x} alloy molecular structure near $x = 0$, 0·33 and 0·4, respectively. For $x = 0{\cdot}33$ or 1/3 the Ge_xSe_{1-x} behaves like a tetrahedrally-bonded glass for which the pressure coefficient of optical gap is positive, which leads to the positive pressure coefficient of resistivity. The initial rise in the resistivity with pressure is due to the $Ge(Se_{1/2})_4$ corner sharing tetrahedra clusters present in $GeSe_2$ glass.

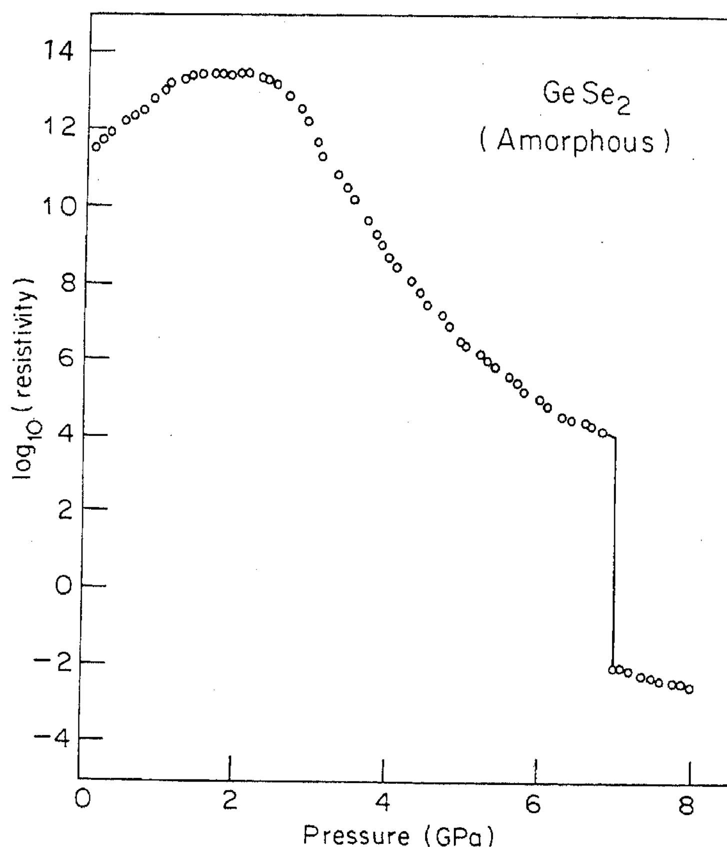

Figure 1. Variation of electrical resistivity of bulk $GeSe_2$ glass as a function of pressure.

Beyond 2·5 GPa, the resistivity decreases exponentially with increase of pressure, which is the behaviour expected for many chalcogenide glasses (Minomura 1982; Parthasarathy *et al* 1984a; Bhatia *et al* 1984).

At 7 GPa the resistivity drops by six orders of magnitude and saturates near a value of $3{\cdot}08 \times 10^{-3}\,\Omega$cm, which is less than the value of the Mott's maximum metallic resistivity (Mott 1970).

The variation of conductivity as a function of temperature at different pressures is shown in figures 2 and 3. It is seen that the conductivity variation obeys the relation $\sigma = \sigma_0 \exp(-E_a/kT)$ where σ_0 is the pre-exponential factor, E_a the activation energy for electronic conduction, k the Boltzmann's constant and T the temperature. At low pressures *i.e.* $p \leqslant 5$ GPa because of the high resistance of the sample the temperature range of investigation is limited to 160 K. At all the pressures, the conduction process is thermally activated with a single activation energy. The value of the pre-exponential factor shows that at all the pressures up to 5 GPa, the conduction in the sample is due to the excitation of the carriers across the mobility edges (Mott 1970).

Figure 4 shows the variation of the normalised resistivity with temperature at 7 and 8 GPa pressures. At both pressures, the temperature coefficient of resistance is positive. The positive temperature coefficient and the numerical value of the resistivity established the existence of the metallic phase at high pressures.

Figure 5 shows the variation of the activation energy as a function of pressure. The activation energy decreases continuously with increase of pressure up to 6 GPa and becomes zero at 7 GPa. The discontinuous changes in the behaviour of the resistivity

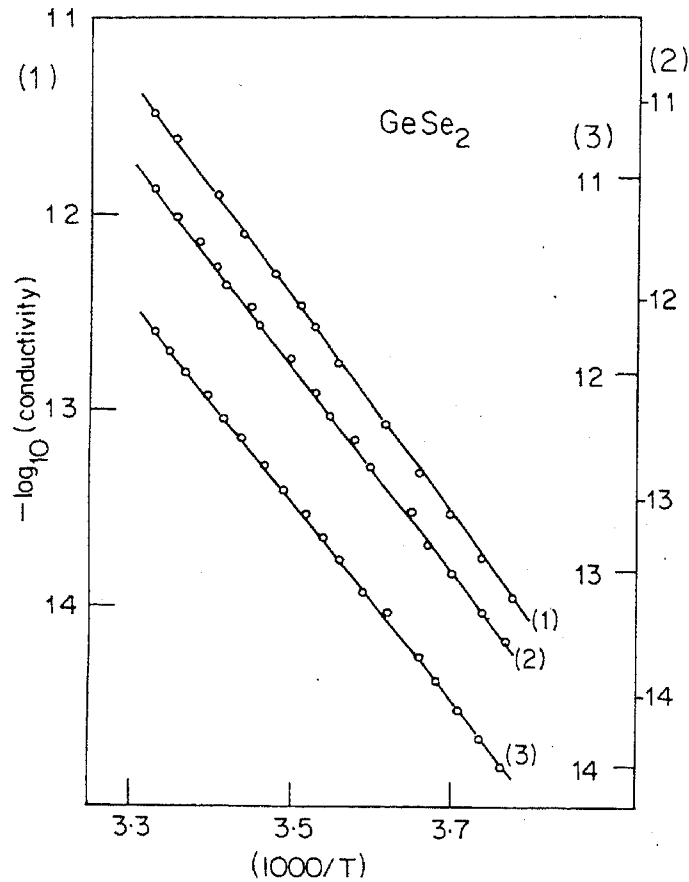

Figure 2. Semi log plot of dc conductivity *vs* $(1000/T)$ for $GeSe_2$ glass at different pressures (Curve 1 for $p = 10^5$ GPa, curve 2 for $p = 1$ GPa, curve 3 for $p = 2$ GPa respectively).

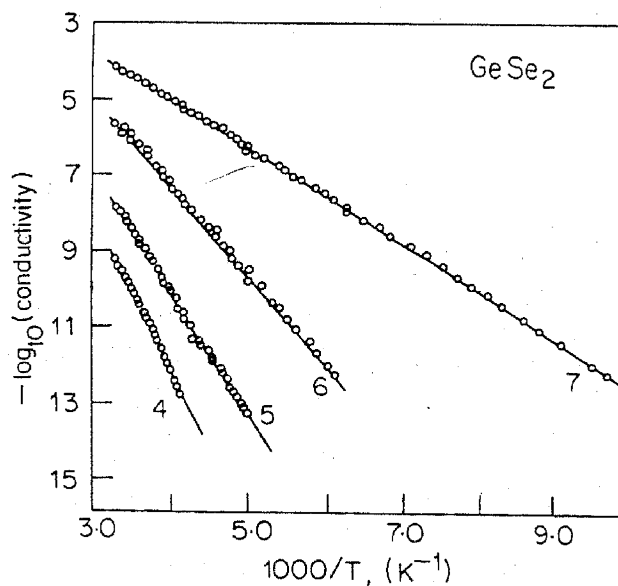

Figure 3. Semi log plot of dc conductivity *vs* $(1000/T)$ for $GeSe_2$ glass at different clamped pressures (curve 4 for $p = 3$ GPa, curve 5 for $p = 4$ GPa, curve 6 for $p = 5$ GPa and curve 7 for $p = 6$ GPa respectively).

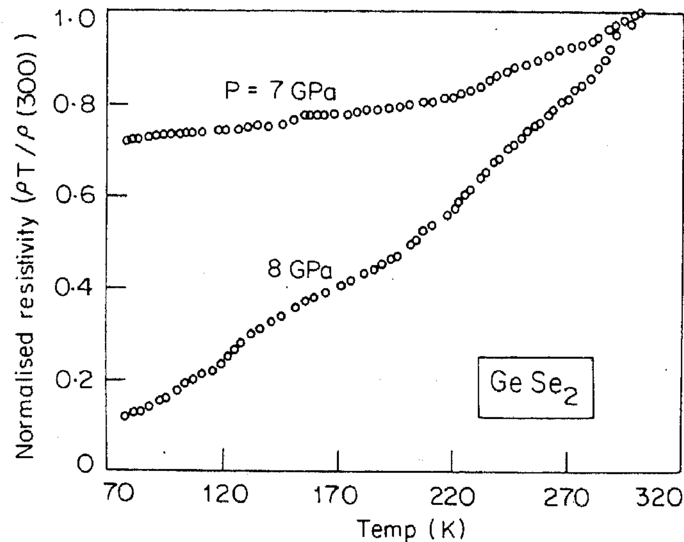

Figure 4. Variation of normalized resistivity $(R(T, P)/R(300\,\mathrm{K}, P))$ as a function of temperature at 7 and 8 GPa pressures.

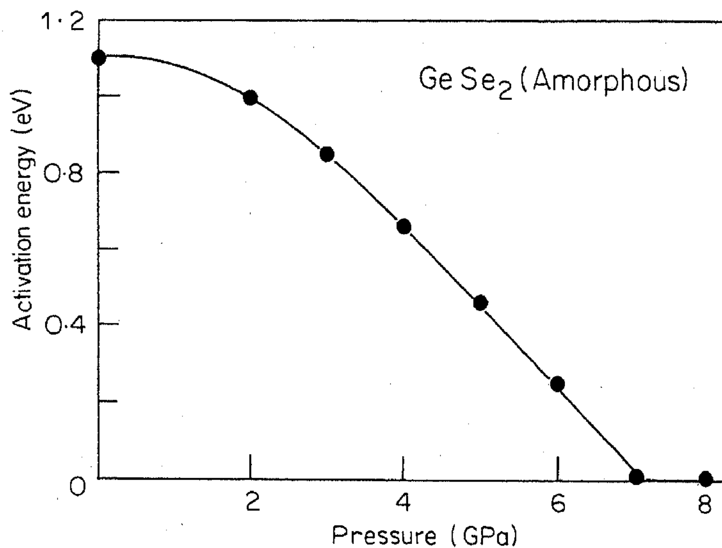

Figure 5. Variation of activation energy (ΔE) as a function of pressure.

with pressure imply that a structural transformation occurs at a pressure of 7 GPa. The x-ray pattern for the sample, which has been pressurised up to 8 GPa is shown in figure 6. The diffraction peaks were indexed except the peak at $2\theta = 79°$ as a face-centred cubic phase with a cell constant $a = 4{\cdot}06$ Å. The peak at $2\theta = 79°$ cannot be indexed as (222) because for $a = 4{\cdot}06$ Å, the line corresponding to (222) will appear at $2\theta = 82°$.

The effect of pressure on the electrical and optical properties of amorphous semiconductors has been reviewed by Minomura (1982). The pressure coefficient of the optical gap in most chalcogenide glasses lies between -1×10^{-1} and -2×10^{-1} eV/GPa. The activation energy E_a derived from the temperature dependence of resistivity and the optical gap E_0, are related by $E_a \simeq \frac{1}{2} E_0$ indicating that the Fermi level lies near the centre of the gap (Sakai and Fritzsche 1977). The value of the pressure coefficient of the activation energy should therefore lie between -5×10^{-2} and -1×10^{-1} eV/GPa. Our experimental values are in good agreement with these values. The

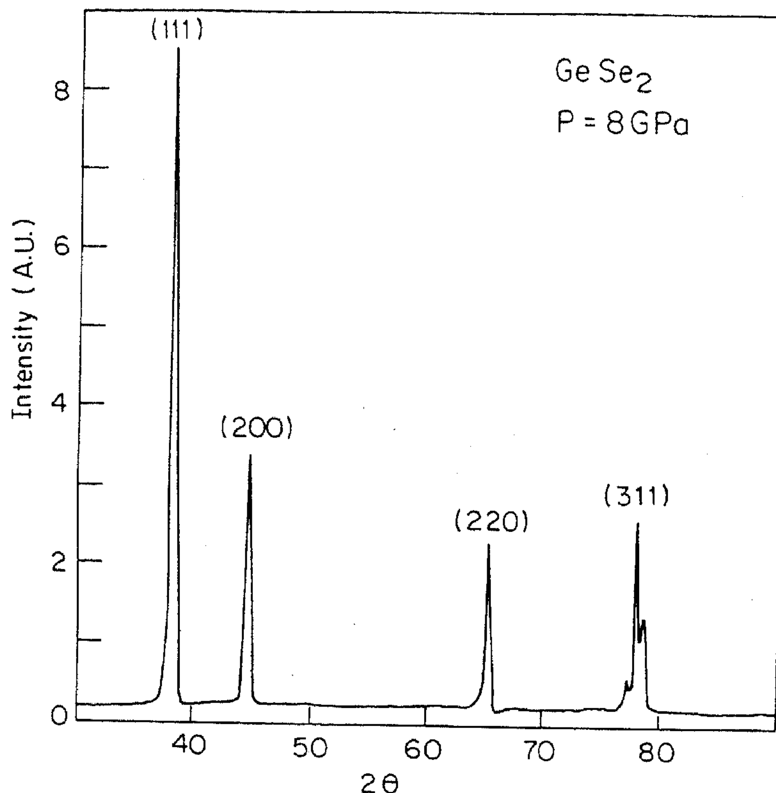

Figure 6. X-ray diffractogram for the pressure quenched $GeSe_2$ samples (samples recovered from the high pressure cell after the application of 8 GPa pressure).

continuous decrease in the activation energy with increase of pressure indicates that the decrease in electrical resistivity (for $P \geqslant 2{\cdot}5$ GPa) under pressure arises from a gradual decrease in the gap. In general the pressure dependence of the electrical resistivity is more complicated, because the resistivity depends not only on the gap but also on the mobility and the position of the Fermi level. Therefore an independent experiment on the pressure dependence of mobility is required to solve some of these problems.

4. Conclusion

We have reported the observation of pressure-induced amorphous semiconductor to crystalline metal transition in bulk $GeSe_2$ glass. The initial rise in the resistivity of the sample with pressure is due to the local nearly tetrahedral molecular clusters in the $GeSe_2$ glass. The activation energy and the resistivity value at 8 GPa confirm the metallic state of the high pressure sample. The x-ray diffraction pattern of the pressure-quenched sample confirms the transition from an amorphous to a fcc structure.

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