JOURNAL OF MATERIALS SCIENCE 32 (1997) 2177–2180

Studies on elemental tellurium under high pressure

J. CHITRALEKHA, E. S. R. GOPAL
Department of Physics, Indian Institute of Science, Bangalore 560 012, India
K. CHATTOPADHYAY
Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

A non-linear behaviour in the resistance of tellurium as a function of pressure has been observed. At each pressure the resistance shows a time variation. At lower pressures, the normalized resistance increases with time, and at higher pressures, the normalized resistance decreases exponentially as a function of time. This change in behaviour with respect to time occurs in the region of the steepest descent in the resistance versus pressure plot. However, the magnitude of the change in the resistance with time is small compared to a change in the resistance with pressure. The origin of this behaviour is suggested to be linked with the generation and annealing of localized charged defects.

1. Introduction

Tellurium is a narrow band gap p-type semiconductor with a bandgap of $E_g = 0.32$ eV. It has been found that under pressure the bandgap of pure tellurium decreases and the element becomes metallic at a pressure of about 40 kbar [1]. The density of states in the valence and conduction band is quite insensitive to pressure, but the hole mobility, as well as the electron mobility, increases with pressure [2]. Hence, the overall effect of pressure is to decrease the resistance.

Bridgman [3] first studied the effect of pressure on the electrical resistance of tellurium up to pressures of 1.2 GPa and at four temperatures from 90–368 K. The resistance of polycrystalline tellurium samples of different purities was also studied by Bridgman [4], and it was found that the factor of the decrease in resistance in the first 3.0 GPa varied from sample to sample. Bridgman attributed such a large variation to the effects of internal strain in this material.

Tellurium has a very low elastic limit at room temperature and has very well-defined cleavage planes of the type $1\,0\,\bar{1}\,0$, which are the prismatic planes. Plastic slip occurs in the planes with the slip direction $a = 1/3\ \langle 2\,\bar{1}\,\bar{1}\,0\rangle$ and $c = \langle 0\,0\,0\,1\rangle$. At room temperature, dislocation glide occurs fairly easily, as the thermal activation barrier is small [5]. Plastic flow occurs due to shear.

The transport properties of tellurium at atmospheric pressure are reported to be strongly dependent on the defect content of the samples. The electrical fields associated with dislocations are strong, and these have strong interactions with charge carriers [6]. The energy bands near the dislocations are highly deformed and electrons become trapped. A relatively low density of the order of 10^6 dislocations/cm^2 is sufficient to trap 10^{13}–10^{14} electrons/cm^3. Saada [6] suggested that the electrical conductivity of the holes in pure tellurium is due to the presence of dislocations.

Recently, high-pressure experiments were conducted in tellurium-rich Ag–Te alloys which yielded a time-dependent behaviour of resistivity change [7]. This prompted a programme of study of the transport behaviour of polycrystalline tellurium under pressure. The aim of this paper is to present and discuss these results.

2. Experimental procedure

High pressure was generated in an opposed anvil apparatus with pyrophillite as the gasket material and steatite as the pressure-transmitting medium. Steatite flows plastically and generates a quasi-hydrostatic medium and isolates the sample (electrically) from the anvil body. Hence at lower pressures the shear is considerable, and at higher pressure the environment is nearly hydrostatic. The details of the apparatus are given elsewhere [7].

Pressure calibration was achieved by standardizing gasket thickness for a particular diameter of the anvil and by plotting the oil pressure (p.s.i.) versus the transition pressure (GPa) of standards like bismuth and ytterbium. The pressure calibration of the system and the experiments was done during the loading cycle.

The tellurium sample was mounted together with an internal calibrant, bismuth, on the steatite disc and four leads each were placed on the sample and calibrant. Both tellurium and bismuth were of similar thickness. A constant current was passed through the outer leads of bismuth and tellurium by two Keithley (model 225) constant current sources. The voltage was measured across the inner two leads. This was done by

0022–2461

connecting the inner two leads of the tellurium sample to one channel of the data logger (Datel PD-10) and the inner two leads of the bismuth sample to another channel of the data logger. The voltage was sampled once every 10 s. The currents used in the high-resistance tellurium samples were of the order of 2.5 mA and the corresponding voltages in the four-probe method were typically of the order of 6 mV. In the case of the low-resistance bismuth, the currents were about 30 mA and the voltages were typically of the order of 75 μV. The Datel PD-10 data logger used for data acquisition has a resolution of ± 1 μV. Thus, for tellurium samples this would correspond to an uncertainity in voltage of 1 part in 6000, as compared to an uncertainity of about 1% in bismuth voltages.

The measuring system enables one to measure the resistance with a time resolution of 0.1 s. The tellurium used in these experiments, was obtained from Nuclear Fuel complex, Hyderabad, India, and is 99.999% pure.

3. Results

Fig. 1 shows the pressure dependence of resistivity observed in polycrystalline tellurium. The resistance shows an initial increase followed by a decrease. The data on resistance are normalized with respect to the initial resistance of the sample at 1 kbar, in all cases. The bismuth resistance versus pressure is also given in the same plot and the inset shows the first pressure transition of bismuth. Bismuth was used as a standard reference for all experimental runs. This acts as a check for the system behaviour of the high-pressure cell.

One of the striking observations of the present work is a time dependence of the resistivity plot. Two distinct types of behaviour were observed. At lower pressures, the resistivity tends to rise with time, and at higher pressures, the resistivity decreases with time. This behaviour is also depicted in Fig. 1, where the beginning of the arrow indicates the initial resistance and the end of the arrow indicates the resistance after 230 s. The normalized resistivity drops rapidly in the intermediate pressure range as can be seen in Fig. 1.

Fig. 2 shows the increase in normalized resistance with time at a lower pressure. Fig. 3 shows the decrease in the normalized resistance of tellurium with time at a higher pressure. The magnitude of the decrease at each pressure (for the same length of time) decreases as the pressure increases. We emphasize that all the samples studied during the course of this investigation exhibit the above described time dependence. However, the percentage change in normalized resistance with respect to time is much smaller compared to that observed with respect to a change in pressure. A better idea of the overall behaviour can be best seen in Fig. 1. As the figure above indicates, the change from one time dependence to the other roughly occurs

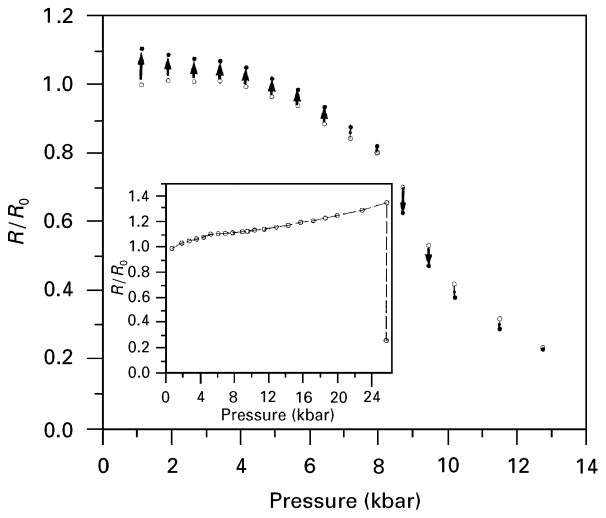

Figure 1 A typical normalized resistance, R/R_0, versus pressure plot for polycrystalline tellurium. The normalization is done with the value at 1 kbar. The arrows mark the direction of resistance change during isobaric hold and the two points at each pressure indicate the resistance value just after pressurization and after 230 s. Also plotted is the normalized resistance of bismuth versus pressure. The inset shows the 2.55 GPa transition of bismuth.

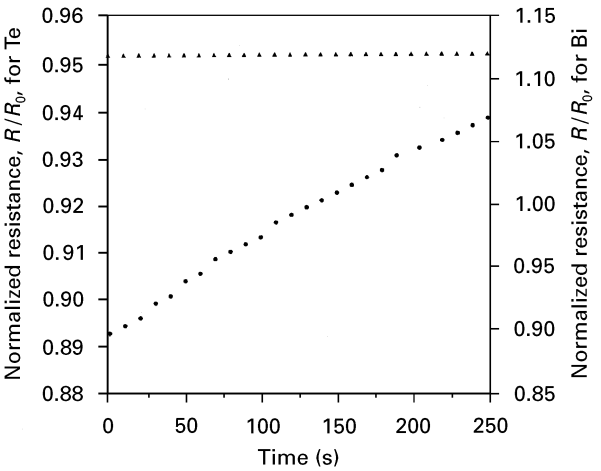

Figure 2 Normalized resistance, R/R_0, versus time for (●) tellurium at a constant pressure of 6.4 kbar showing an increase in resistance with time. Also plotted is the normalized resistance of bismuth (▲) at the same pressure. Note the uncertainity in the value of the normalized resistance of bismuth is of the order of 1%, as discussed in the text.

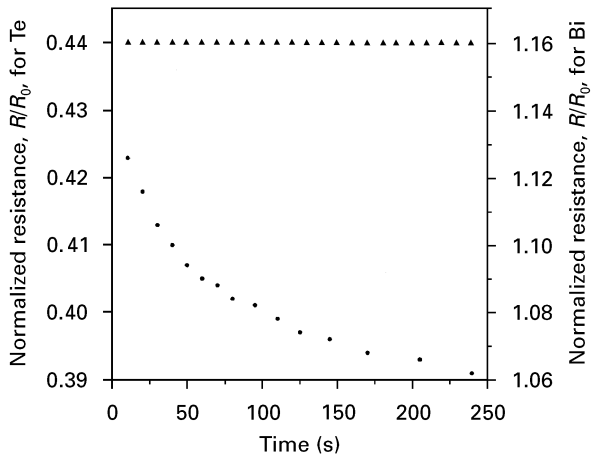

Figure 3 Normalized resistance, R/R_0, versus time for (●) tellurium at a constant pressure of 10 kbar showing a decrease in resistance with time. Also plotted is the normalized resistace of bismuth at the same pressure. Note the uncertainity in the value of the normalized resistance of bismuth (▲) is of the order of 1%, as discussed in the text.

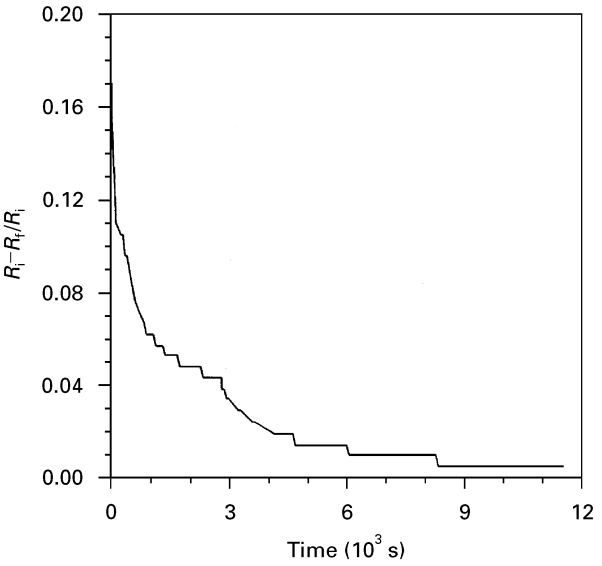

Figure 4 A plot of $R_i - R_f/R_i$ versus time for tellurium at a constant pressure of 11.5 kbar, showing the steady state of resistance at that pressure.

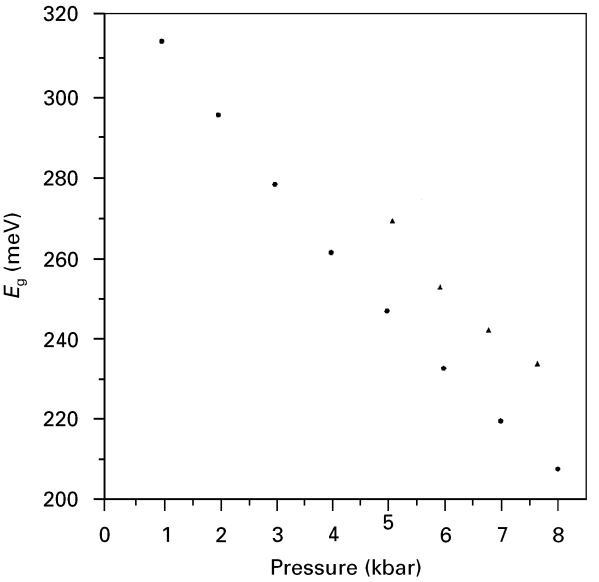

Figure 5 (▲) Band gap as a function of pressure for tellurium obtained using the current data extrapolated to infinite time, with the E_g at 1 kbar taken from Kosichkin [8]. (●) The data of Pines *et al.* [9] plotted for comparison.

near the middle of this curve where the slope is the steepest.

In order to confirm further the time-dependent behaviour of the resistivity, we carried out experiments at a constant pressure until equilibriation. Fig. 4 shows the result at 11.5 kbar where the fraction change from initial resistance, R_i, is plotted as a function of time. R_f is the final resistance.

4. Discussion

As can be seen from Fig. 4, the resistance achieves a steady-state value at each pressure only after a few hours. Most of the normalized resistance values presented in this study are non-steady-state values, i.e. they have been observed for a limited time only. When the resistance achieves a steady-state value, at each pressure the number of charge carriers and their mobility are constant. It is of interest to see if the data are extrapolated to infinite time value, whether the situation is similar to the steady-state situation, and whether the experimental bandgap values can be recovered. A curve fitting was done only for higher pressures where the resistance values are decaying. An exponential function of the form

$$R = [R_0 - R_\infty]\exp[-kt] + R_\infty \qquad (1)$$

was used, where R_∞ is the resistance at infinite time.

Using the R_∞ value of this fit at each pressure, we have calculated the bandgap of tellurium. The value of the bandgap at 1 kbar has been taken from Kosichkin [8]. Fig. 5 gives the plot of $E_g(P)$ versus P. Also plotted for comparison are the data of Pine *et al.* [9]. The curve observed by this procedure is similar to the experimental data of Pine *et al.*, although the absolute values seem to be slightly higher.

Before further discusion, we first summarize the main observations of the present investigation. The resistivity of the sample decreases with pressure in the range 0–15 kbar. The decrease is highly non-linear and the curve looks like an inverted S with a steep fall of resistivity in a narrow domain. The resistivity also exhibits a time dependence with an increasing trend at lower pressures. At higher pressures, the resistivity decays with time. The crossover from one type to another, approximately coincides with the steepest change in the resistivity curve.

In order to explain the present results, we first note that the relaxation in stress patterns in the pressure-transmitting medium (in this type of experiment) is a possible explanation for this behaviour. However, in the case of the present experiment, the above explanation is not valid, because bismuth, which is under identical conditions to the tellurium, does not show any time dependence.

Although a decrease in the band gap could explain the main features of the sharp fall of resistivity observed in our experiments, the time dependence of resistivity cannot be explained. It is more likely that the observed behaviour is linked to defect states.

It is well known that defects, such as dislocations, have a very strong effect on the electrical transport properties of tellurium [10]. The cores of the dislocations are highly charged and in tellurium, due to the large polarizability of the atom, the electric field associated with the dislocation has a long range. This gives rise to piezo-scattering. Electon microscopic observations of dislocations in uniaxially compressed tellurium samples indicate that the dislocation distribution is heterogenous (varies from 10^6–10^{10} cm^2 at various locations in the same sample subjected to compression) [11]. Further, as the deformation rate increases, the number of dislocations also increases.

Experiments have been carried out to study the influence of plastic deformation on the electrical transport properties and galvanomagnetic properties of tellurium single crystals. The transport properties are strongly dependent on the defect content of the

samples [12]. The resistivity of a plastically deformed sample increases with time by a few orders of magnitude on annealing at room temperature. It has also been observed that carrier density increases initially due to plastic deformation. On annealing at room temperature, a decay with respect to time obeying an approximately exponential law with a time constant of about 100 h, was observed. The initial increase in resistivity has been attributed to piezo-scattering associated with the stress field of dislocations. It is shown that this is an important effect which influences scattering process and often dominates over other effects associated with dislocations in tellurium.

In fact, such a time-dependent behaviour in resistance under pressure has been observed in several glassy systems, such as $In_{20}Te_{80}$, $Cu_{25}Au_5Te_{70}$ [13], arsenic [14], bulk and thin-film phosphorus [15, 16], InSb [17], AsTe, AsTeIn and AsTeGe [18]. These have been observed under various pressure conditions. In all these cases, resistivity drops with time similar to the current results at higher pressures. Various explanations related to the presence of different defect states have been proposed as the cause for such a behaviour. An order of magnitude increase in the number of defect states has been observed in amorphous phosphorus on an increase in pressure from 44 kbar to 61.5 kbar [15, 16]. In several of these results, resistivity data can be fitted to a relation of the form $R_\infty \ln t$ [18].

The time-dependent behaviour clearly indicates a defect-related process influencing the transport behaviour in polycrystalline tellurium. Although direct evidence of such a process and identification of the specific defect could not be achieved in the present investigation, it is possible to speculate on the probable nature of such defects. Clearly two types of competing defect behaviour are necessary to explain the observed behaviour. In the low-pressure regime, the defect strongly scatters the carrier, resulting in a rise in resistivity. The time-dependent rise points to a complex evolution of these scattering centres. This result is consistent with the results of plastic deformation where a similar increase in resistivity and decrease in carrier concentration were earlier observed [12]. The results therefore suggest the possible role of a non-hydrostatic component which exists in our high-pressure apparatus. The time-dependent decay suggests that the defect relaxation process is both a function of pressure and time. At higher pressures the influence of the defect flattens out.

5. Conclusion

The normalized resistance of tellurium as a function of pressure shows a non-linear behaviour and the resistance at each pressure shows a time-dependent behaviour. For low pressures, the resistance increases with time, while at higher pressures it decreases with time. This change in behaviour occurs in the region of the steepest descent in the resistance versus pressure plot. The resistance values for tellurium at each pressure have been extrapolated to infinite time value and this has been further used to calculate the band gap, which is then compared with the other experimental values. The calculated band gap by the above extrapolation was found to be higher than the experimental values. An explanation on the basis of the creation and annihilation of charged defects, is suggested. This is supported by the reported behaviour during plastic deformation of tellurium.

Acknowledgement

The authors thank Dr S. S. K. Titus, Dr S. Asokan and Mr R. Ramakrishna for help with the experiments and many stimulating discussions.

References

1. J. BARDEEN, *Phys. Rev.* **75** (1949) 1777.
2. D. LONG, *ibid.* **101** (1956) 1256.
3. P. W. BRIDGMAN, *Proc. Am. Acad. Arts Sci.* **68** (1933) 95.
4. *Idem*, *ibid.* **82** (1953) 83.
5. J. P. ESTIENNE and J. L. FARVACQUE, *Phys. Status Solidi* (*a*) **49** (1978) K109.
6. G. SAADA, *Phys. Status Solidi* (*b*) **44** (1971) 717.
7. CHITRALEKHA JACOB, PhD thesis, Indian Institute of Science, Bangalore (1993).
8. Yu. V. KOSICHKIN, in "The Physics of Selenium and Tellurium", (edited by E. Gerlach and P. Grosse), Springer, Berlin, (1979) p. 95.
9. A. S. PINE, N. MENYUK and G. DRESSELHAUS, *Solid State Commun.* **31** (1979) 187.
10. J. C. DOUKHAN, R. DROPE, J. L. FARVACQUE, E. GERLACH and P. GROSSE, *Phys. Status Solidi* (*b*) **64** (1974) 237.
11. A. BRONIATOWSKI and G. FAIVRE, *Philos Mag.* **30** (1974) 765.
12. G. FAIVRE, *ibid.* **29** (1974) 1289.
13. S. T. LAKSHMIKUMAR, V. C. PADAKI, R. M. MALLYA and E. S. R. GOPAL, *J. Non. Cryst. Solids* **46** (1981) 33.
14. S. R. ELLIOT, E. A. DAVIES and G. D. PITT, *Solid State Commun.* **22** (1977) 481.
15. P. EXTANCE and S. R. ELLIOT, *Philos. Mag. B* **43** (1981) 469.
16. *Idem*, *ibid.* **43** (1981) 485.
17. O. SHIMOMURA, K. ASOUMI and N. SAKAI, *ibid.* **34** (1976) 839.
18. R. T. JOHNSON and R. K. QUINN, *J. Non-Cryst. Solids* **28** (1978) 273.

Received 11 April 1995
and accepted 12 August 1996