

## The p-n transition in molten Ge-Te-M alloys (M identical to Tl or Bi)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 8523

(<http://iopscience.iop.org/0953-8984/5/45/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 02:13

Please note that [terms and conditions apply](#).

## The p–n transition in molten Ge–Te–M alloys (M≡Tl or Bi)

Hiroshi Hashimoto and Yoshio Nakamura

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Received 3 August 1993

**Abstract.** The electrical conductivity and thermoelectric power of the molten semiconductor alloy systems Ge–Te–M (M≡Tl or Bi) have been measured as functions of composition and temperature. In accordance with the behaviours already found in the corresponding glassy systems, the addition of Bi to molten Ge–Te alloys causes a conversion to n-type conduction at a relatively small Bi concentration (5–10 at.%), while the addition of Tl preserves the p-type conduction up to a high Tl concentration. In the molten GeTe<sub>4</sub>–Tl system a p–n transition occurs at 61.5 at.% Tl, where the conductivity shows a sharp minimum.

### 1. Introduction

It is known that most chalcogenide alloy glasses prepared by quenching from the melt are p-type conductors and that the conversion to n-type conduction by the addition of a relatively small amount of dopants is usually difficult. Tohge *et al* [1, 2], however, have shown that n-type semiconducting glasses were obtained by adding Bi to Ge–Se and Ge–Se–Te glasses [1, 2]. This special effect of Bi on the p–n conversion of chalcogenide glass semiconductors has been confirmed later in other systems such as Ge–S–Bi [3] and Ge–Te–Bi [4]. The origin of this anomalous behaviour of Bi in the carrier-type reversal in these chalcogenide glasses has been discussed by several workers [2, 3, 5, 6]. Among them, Nagels and co-workers [3] proposed a model based upon percolation-controlled conduction by n-type crystallites Bi<sub>2</sub>X<sub>3</sub> (X≡chalcogen element) existing in ‘inhomogeneous’ glass samples. However, the microscopic mechanism of the p–n transition in this class of materials still remains controversial and is far from being well understood. We think a similar investigation of liquid materials will be highly interesting in order to elucidate the origin of the special behaviour of Bi in glassy materials.

In a previous paper [7], we have reported that the totally different behaviours of Bi and Tl are found in the addition to ‘liquid’ As<sub>2</sub>Te<sub>3</sub>. As found in germanium chalcogenide glasses, the conduction type of molten As<sub>2</sub>Te<sub>3</sub> is converted from p- to n-type by adding a relatively small amount of Bi, while the addition of Tl changes the conduction type only with a very large amount of Tl, i.e. 54.5 at.% Tl. No similar observation was possible on glassy samples of the As<sub>2</sub>Te<sub>3</sub>–Bi and As<sub>2</sub>Te<sub>3</sub>–Tl systems because of the difficulty of vitrification of these systems. In the present study, we have measured the electrical conductivity and thermoelectric power of some germanium–tellurium alloys doped or modified with the metallic elements Tl, Bi or Pb, on which some measurements in the glassy state have already been reported [4].

## 2. Experimental details

Sample alloys were prepared from the constituent elements Ge (purity, 99.999%), Te (purity, 99.9999%), Tl (purity, 99.99%), Bi (purity, 99.9999%) and Pb (purity, 99.9999%), sealing and melting them in an evacuated glass ampoule at 550 °C for 1 or 2 d. The conductivity was measured by the four-probe method in a U-type capillary cell with tungsten electrodes. The thermoelectric power was determined from the electromotive force due to the temperature gradient between the two measuring electrodes, which was generated by a supplementary heater. The counter-electrode correction was made using the reported data for tungsten [8]. The accuracy of the observed electrical conductivity was within  $\pm 0.5\%$  and that of the thermoelectric power within  $\pm 5\%$ . The compositions of the sample mixtures were determined from the weights of the components, which was accurate to within  $\pm 0.2\%$ . The temperature range of measurements was from the melting point of each sample to about 600 °C. The temperature was controlled to within  $\pm 0.5$  °C.

## 3. Results

Figure 1 shows the electrical conductivity and thermoelectric power of  $\text{Ge}_{20}\text{Te}_{80-x}\text{Tl}_x$  and  $\text{Ge}_{20}\text{Te}_{80-x}\text{Bi}_x$  alloys at 873 K. It is found that the addition of Bi converts the conduction type at a relatively low concentration of Bi, i.e. about 5 at.%, in good agreement with the results for glassy samples of the same system, in which the p-n transition has been observed at the composition with  $x = 3.5$  [4]. On the other hand, the addition of Tl causes no such effect on the thermoelectric power, which is positive and rather increases with increasing Tl concentration. The solubilities of the added elements Tl and Bi in the above two systems are rather limited in the present range of experimental temperatures to make measurements over a wider concentration range up to  $x = 80$ . Viewing these preliminary experimental results on  $\text{Ge}_{20}\text{Te}_{80-x}\text{M}_x$  melts, we chose the pseudo-binary systems  $\text{GeTe}_4$ -Tl and  $\text{GeTe}_4$ -Bi, or more specifically  $(\text{Ge}_{20}\text{Te}_{80})_{1-y}\text{Tl}_y$  and  $(\text{Ge}_{20}\text{Te}_{80})_{1-y}\text{Bi}_y$  systems. This enables us to measure the electrical conductivity and thermoelectric power over the entire concentration range  $y$  of the respective systems, as already done for the molten  $\text{As}_2\text{Te}_3$ -Tl and  $\text{As}_2\text{Te}_3$ -Bi systems [7]. The experimental results for the electrical conductivity  $\sigma$  and the thermoelectric power  $S$  in the molten  $\text{GeTe}_4$ -Tl system are shown in figures 2 and 3, respectively, as functions of temperature. The results for the molten  $\text{GeTe}_4$ -Bi system are shown in figures 4 and 5. Figure 6 shows the composition dependence of the electrical conductivity of the molten  $\text{GeTe}_4$ -Tl and  $\text{GeTe}_4$ -Bi systems at 873 K. As found in the corresponding  $\text{As}_2\text{Te}_3$ -M systems, the electrical conductivity increases monotonically on the addition of Bi, while it decreases first on the addition of Tl. The minimum of the electrical conductivity in the  $\text{GeTe}_4$ -Tl system is located at around 60 at.% Tl. The conductivity then increases rapidly with increasing Tl concentration and finally shows metallic behaviour. Figure 7 shows the results for the thermoelectric power of the two systems at 873 K. In figures 6 and 7 the values of  $\sigma$  and  $S$  for pure Tl and Bi are taken from the literature [9, 10]. The behaviour of  $S$  in the present  $\text{GeTe}_4$ -M systems is also quite similar to that in  $\text{As}_2\text{Te}_3$ -M. The addition of Bi changes the sign of  $S$  at a relatively low metal concentration, i.e. at about 5 at.% Bi. On the other hand, the addition of Tl causes a p-n transition at about 60 at.% Tl, where the electrical conductivity shows a minimum. The effect of the addition of Pb on the electrical conductivity and the thermoelectric power has also been examined, as shown in figures 6 and 7, respectively. As the solubility of Pb in the present experimental temperature range was very small, results at a single concentration, 5 at.%, are

given. The present results for Pb addition are rather close to those for Tl addition. Tohge *et al* [11] have shown that the p-n transition in chalcogenide glasses due to the Pb addition occurs at much higher concentrations of Pb, such as at  $x = 21$  in  $\text{Pb}_{20}\text{Ge}_x\text{Se}_{80-x}$ .

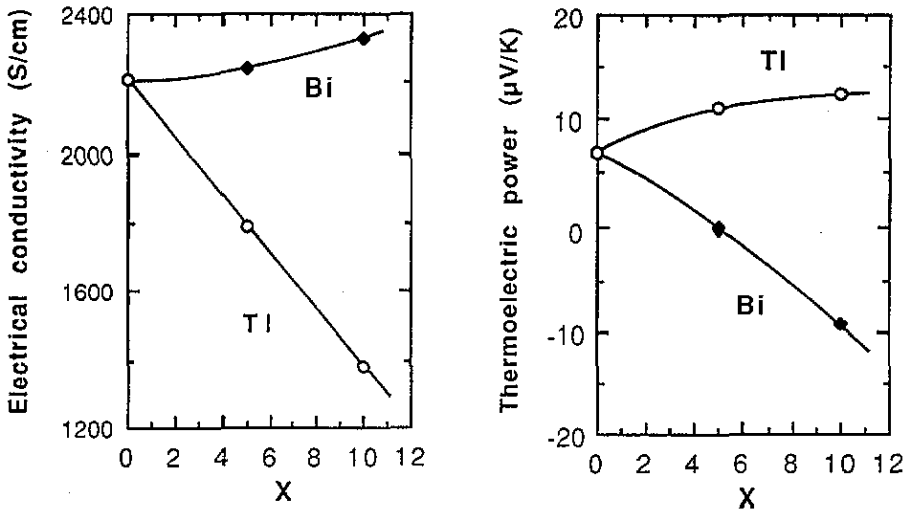


Figure 1. Electrical conductivity and thermoelectric power of molten  $\text{Ge}_{20}\text{Te}_{80-x}\text{Tl}_x$  and  $\text{Ge}_{20}\text{Te}_{80-x}\text{Bi}_x$  at 873 K.

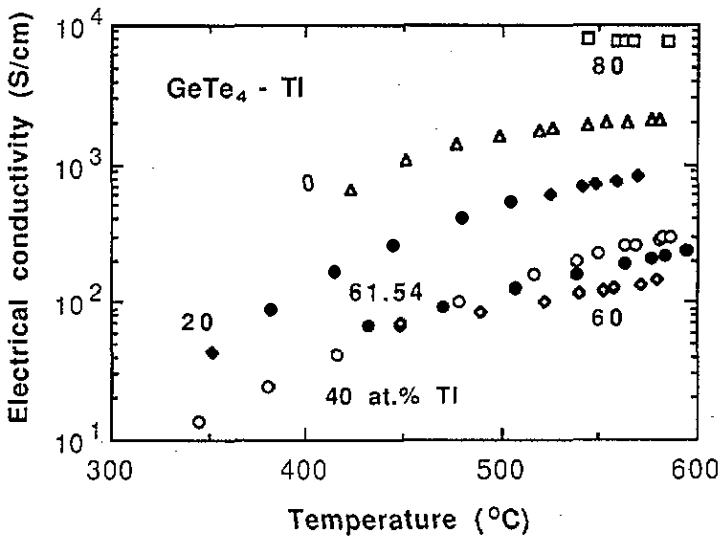


Figure 2. Temperature dependence of the electrical conductivity of the molten  $\text{GeTe}_4\text{-Tl}$  system.

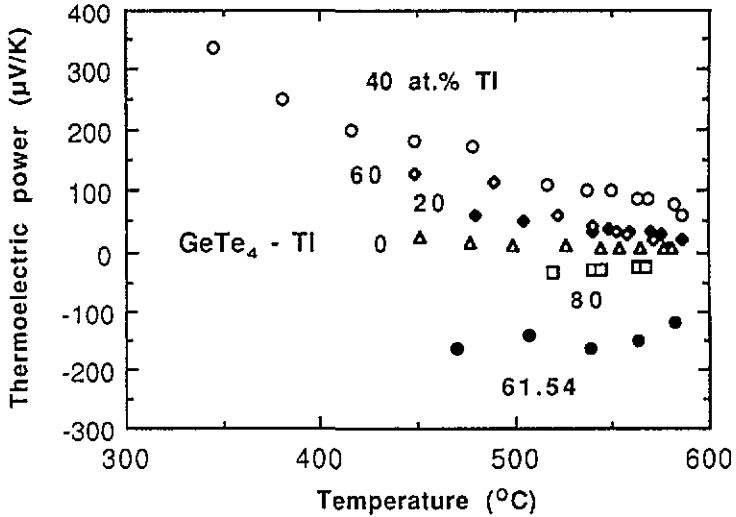


Figure 3. Temperature dependence of the thermoelectric power of the molten  $\text{GeTe}_4\text{-Tl}$  system.

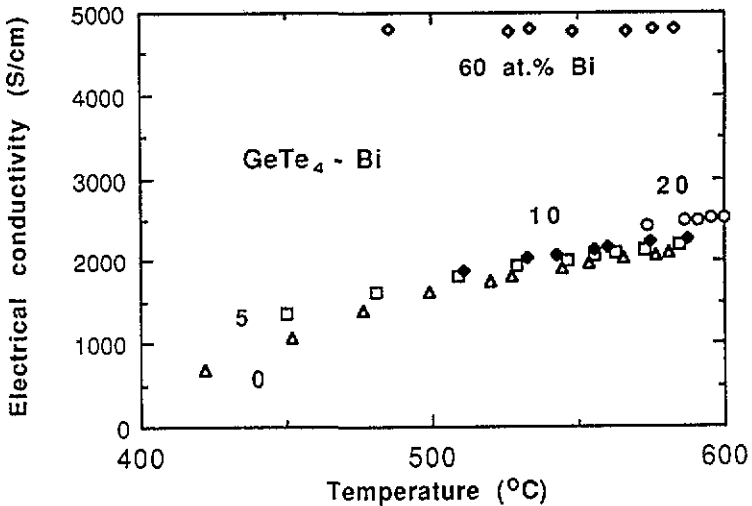
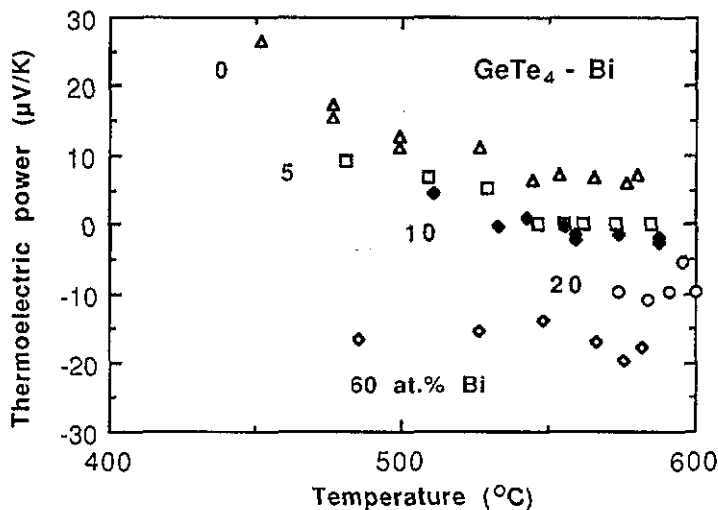
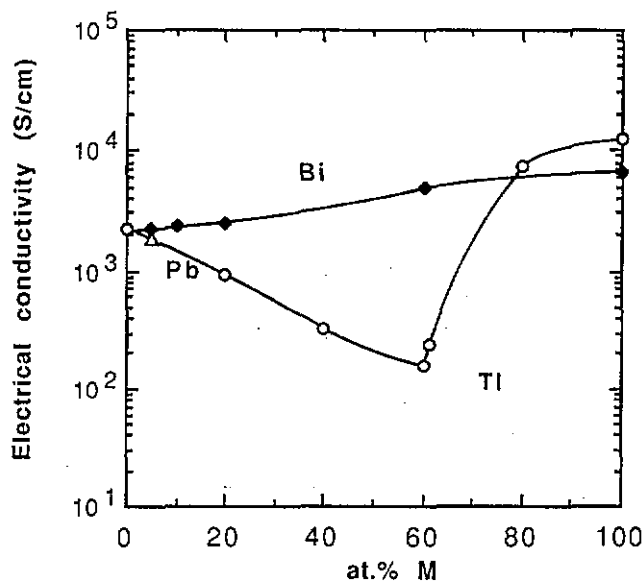


Figure 4. Temperature dependence of the electrical conductivity of the molten  $\text{GeTe}_4\text{-Bi}$  system.

#### 4. Discussion

It is now generally accepted that the conduction mechanism in liquid semiconductors, as well as in amorphous semiconductors, can be described in terms of the mobility edge model [12]. The conductivity is almost zero in the energy range  $E_v < E < E_c$ . The position of the Fermi energy  $E_F$  relative to the mobility edge  $E_c$  of the conduction band, or the mobility edge  $E_v$  of the valence band, determines the type of dominant carriers. When the separation  $E_F - E_v$  between  $E_F$  and  $E_v$  is smaller than  $E_c - E_F$ , the conduction is dominated by holes. The conduction is electronic in the opposite case. The first detailed quantitative estimation of the effect of the shift of  $E_F$  on the electrical conductivity  $\sigma$  and


 Figure 5. Temperature dependence of the thermoelectric power of the molten GeTe<sub>4</sub>-Bi system.

 Figure 6. Composition dependence of the electrical conductivity of the molten GeTe<sub>4</sub>-M systems at 873 K. M:Ti (○), Pb (△), and Bi (◆).

thermoelectric power  $S$  of liquid semiconductors has been given by Barnes *et al* [13] on the basis of the Kubo-Greenwood equations, together with the Fermi-Dirac distribution function. They assumed a linear energy dependence of the conductivity as

$$\sigma(E) = \begin{cases} \alpha_v(E_v - E) & E < E_v \\ \alpha_c(E - E_c) & E > E_c \end{cases}$$

and gave numerical estimates of values of  $\sigma$  and  $S$  as functions of the parameters  $\alpha_v$ ,  $\alpha_c$ ,  $E_v$ ,  $E_c$  and  $E_F$  [12].

In the molten GeTe<sub>4</sub>-Bi system, the addition of Bi causes a shift in  $E_F$  towards the conduction band edge more rapidly than in the molten GeTe<sub>4</sub>-Ti system. The former

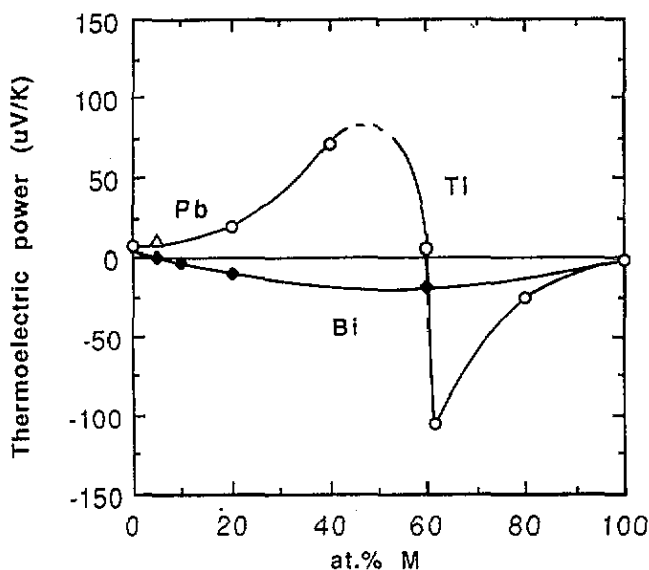
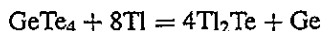


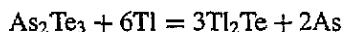
Figure 7. Composition dependence of the thermoelectric power of the molten  $\text{GeTe}_4\text{-M}$  systems at 873 K. M: Tl (O), Pb ( $\Delta$ ), and Bi ( $\blacklozenge$ ).

system becomes unipolar conductor as  $E_c - E_F$  approaches zero and then metallic in the region where  $E_F > E_c$ . On the other hand, in the molten  $\text{GeTe}_4\text{-Tl}$  system, the Fermi level moves more gradually towards the centre of the gap, the mobility gap structure remaining rather unchanged. The S-shaped composition dependence of the thermoelectric power of this system is well explained by the picture given by Enderby and Barnes [12]. According to them, the mobility gap  $\Delta E (= E_c - E_v)$  can be estimated from the peak-to-peak thermoelectric power  $\Delta S$ , which is about  $200 \mu\text{V K}^{-1}$  for the present  $\text{GeTe}_4\text{-Tl}$  system at 873 K, as shown in figure 7. This corresponds to a gap value of  $\Delta E = 0.1 \text{ eV}$ . A similar value of  $\Delta E$  is obtained for the molten  $\text{As}_2\text{Te}_3\text{-Tl}$  system studied previously [7]. As we cannot determine the values of the conduction parameters given above from the conductivity data alone, we leave for the time being the present argument at a qualitative level.

Now we consider the origin of the different behaviours of Bi and Tl. The composition dependences of the electrical conductivity and thermoelectric power of the molten  $\text{GeTe}_4\text{-Tl}$  system strongly suggest the existence of a rigid mobility edge in the p-type region. The p-n transition takes place at a certain stoichiometric composition. We assume that the chemical reaction



occurs and is completed when Ge-Te bonds are totally converted to Tl-Te bonds. This composition corresponds to the atomic fraction of Tl,  $8/(5+8) = 0.615$ , and exactly to the composition where the drastic changes in  $\sigma$  and  $S$  were observed. A quite similar behaviour has already been found in the molten  $\text{As}_2\text{Te}_3\text{-Tl}$  system, in which the reaction



is completed at the composition with the atomic fraction of Tl,  $6/(5+6) = 0.545$ , or 54.5 at.% Tl, where the p-n transition and the minimum in  $\sigma$  have been found [7]. These results indicate that the strong interaction of Tl and Te breaks up the Ge-Te or As-Te bonds to

complete short-range order around Tl atoms up to the respective stoichiometric compositions mentioned above. The excess Tl above the stoichiometric compositions acts as a donor and raises the transition to n-type conduction and subsequent metallization. A neutron diffraction study on molten Tl-As<sub>2</sub>X<sub>3</sub> (X≡Se or Te) by Uemura and co-workers [14] shows that the peak due to As-Te bonds in molten Tl-As<sub>2</sub>Te<sub>3</sub> disappears with increasing Tl concentration, prior to the bulk metallization, while more covalent As-Se bonds remain unchanged up to a high Tl concentration. This structural information is in accordance with our present interpretation.

On the other hand, the bonding of Bi and Te is not strong enough to preserve the short-range order around Bi and the melts behave as ordinary metallic alloys of Bi-Ge-Te. The effect of inhomogeneity associated with possible microcrystallite formation was not detectable in the Bi-GeTe<sub>4</sub> melts. The relatively weak interaction between Bi and the chalcogen elements X in the molten Bi<sub>2</sub>X<sub>3</sub> is manifested in their high electrical conductivity of the order of 1000–3000 S cm<sup>-1</sup>, which is much larger than those of molten Tl<sub>2</sub>X, 10–100 S cm<sup>-1</sup> [12, 15]. The static structures around the doped elements Bi and Tl in the melts, as well as their thermodynamic activities, will be the subject of future investigation.

## 5. Summary

We have measured the electrical conductivity and thermoelectric power of some molten Ge-Te-M alloys (M≡Tl or Bi), paying attention to the p-n transition. In molten Ge<sub>20</sub>Te<sub>80-x</sub>M<sub>x</sub> alloys, a change to n-type conduction has been found on the addition of about 5 at.% Bi at 873 K, while no sign of the carrier-type conversion was observed on adding Tl in a similar concentration. This is in agreement with the observation for the corresponding glass materials [4]. In the molten GeTe<sub>4</sub>-M (M≡Tl or Bi) systems at 873 K, a p-n transition has been found at about 10 at.% Bi and 61.5 at.% Tl, respectively. These results indicate that the conversion to n-type conduction at a relatively low concentration of Bi is due to the interaction of Bi and Te which is much weaker than that of Tl and Te.

## Acknowledgments

The authors acknowledge financial support from the Nippon Sheet Glass Foundation for Materials Science. They also wish to thank Mr T Kiya for his technical assistance.

## References

- [1] Tohge N, Minami T and Tanaka M 1977 *Japan. J. Appl. Phys.* **16** 977
- [2] Tohge N, Minami T, Yamamoto Y and Tanaka M 1980 *J. Appl. Phys.* **51** 1048
- [3] Tichy L, Ticha H, Triska A and Nagels P 1985 *Solid State Commun.* **53** 399
- [4] Bhatia K L, Parthasarathy G, Sharma A and Gopal E S R 1988 *Phys. Rev.* **38** 6342
- [5] Elliott S R and Steel A T 1987 *J. Phys. C: Solid State Phys.* **20** 4335
- [6] Phillips J C 1987 *Phys. Rev. B* **36** 4265
- [7] Nakamura Y, Hiruta M and Hashimoto H 1990 *J. Non-Cryst. Solids* **117–8** 289
- [8] Cusack N and Kendall P 1958 *Proc. Phys. Soc.* **72** 898
- [9] Wilson J R 1965 *Met. Rev.* **10** 381
- [10] Marwaha A S 1967 *The Properties of Liquid Metals* ed P D Adams *et al* (London: Taylor & Francis) p 617
- [11] Tohge N, Matsuo H and Minami T 1987 *J. Non-Cryst. Solids* **95–6** 809
- [12] Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85



- [13] Barnes A C, Laundry D and Enderby J E 1987 *Phil. Mag.* B 55 497
- [14] Sugawara Y, Mineta N and Uemura O 1992 *Proc. Ann. Meet. of Japan Institute of Metals* (Tokyo: Japan Institute of Metals) p 731
- [15] Cutler M 1977 *Liquid Semiconductors* (New York: Academic) p 13