



PRESSURE-INDUCED SEMICONDUCTOR-TO-METAL TRANSITION IN LIQUID Te-Se MIXTURES

M. Yao, K. Suzuki, H. Hoshino, H. Endo

► To cite this version:

M. Yao, K. Suzuki, H. Hoshino, H. Endo. PRESSURE-INDUCED SEMICONDUCTOR-TO-METAL TRANSITION IN LIQUID Te-Se MIXTURES. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-28-C8-31. 10.1051/jphyscol:1980807 . jpa-00220191

HAL Id: jpa-00220191

<https://hal.science/jpa-00220191>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

PRESSURE-INDUCED SEMICONDUCTOR-TO-METAL TRANSITION IN LIQUID Te-Se MIXTURES

M. Yao, K. Suzuki*, H. Hoshino** and H. Endo

Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan.

**College of General Education, University of Tokyo, Tokyo 153, Japan.*

***Faculty of Education, Hirosaki University, Hirosaki 036, Japan.*

Abstract.— The electrical conductivity σ , the thermoelectric power S and the sound velocity C have been measured for liquid Te-Se mixtures in a wide temperature and pressure range. Substantial changes in σ and S from semiconducting to metallic values are induced by a slight application of pressure. The region where such changes occur is determined on the concentration-temperature plane and in that region the prominent maxima in the temperature variations of compressibility appear. It is suggested that the observed semiconductor-to-metal transition is originated from the structural change.

INTRODUCTION— A number of experiments have demonstrated that the electronic properties of liquid Te-Se mixtures change substantially with temperature and concentration. The mixtures with Se-rich concentration exhibit semiconducting behaviour at low temperatures. With increasing Te concentration or increasing temperature the semiconducting nature changes towards metallic. Liquid Se is known to contain chain molecules derived from two-fold covalently bonded atoms together with dangling-bond atoms, and the character of bonding among these chain molecules is van der Waals type. By addition of Te atoms, the concentration of threefold bonded atoms increases and when it becomes a sufficient amount the metallic character appears. Since such chain structure with anisotropic bonds is expected to be transformed to the structure with more isotropic bonds by changing pressure and temperature, it is interesting to study the electronic and thermodynamic properties of the liquid Te-Se mixtures at various pressures

and temperatures. In this paper, we report the results of the electrical conductivity σ , the thermoelectric power S and the sound velocity C of liquid Te-Se mixtures under high pressures.

EXPERIMENTAL PROCEDURES— The electrical conductivity of liquid Te-Se mixtures has been measured in the pressure range 2–25 kbar by using the piston cylinder method up to 650°C and in the pressure range 0–1 kbar by using an internally heated autoclave up to 1600°C. The thermoelectric power S has been measured simultaneously with σ at the lower pressures (0–1 kbar). The sound velocity in liquid Te-Se mixtures has been measured by the ultrasonic pulse transmission/echo technique near the atmospheric pressure up to 800°C and the adiabatic compressibility β_s has been estimated by using density data[1]. The measurement of C under high pressures has been done by using the piston cylinder apparatus up to 10 kbar and up to 600°C. Further experimental details are described elsewhere[2,3].

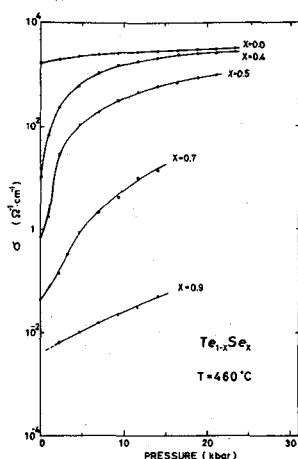


Fig. 1. Pressure variation of σ for liquid Te-Se mixtures at 460°C.

RESULTS AND DISCUSSION-- Figure 1 shows the pressure variations of σ for liquid Te-Se mixtures at 460°C. The pressure variation of σ for liquid pure Te is small. For liquid $\text{Te}_{60}\text{Se}_{40}$ and $\text{Te}_{50}\text{Se}_{50}$ mixtures, σ increases rapidly with pressure in a relatively low pressure region (< 5 kbar) and reaches nearly metallic values ($300 \text{ ohm}^{-1} \text{ cm}^{-1}$) at high pressures. The rate of increase in σ is reduced by further addition of Se.

Figure 2 shows the values of $(\partial \ln \sigma / \partial P)_T$ and $(\partial \ln S / \partial P)_T$ for a liquid $\text{Te}_{50}\text{Se}_{50}$ mixture at 100 bar as a function of temperature. Broad maxima are seen around 600°C in both $(\partial \ln \sigma / \partial P)_T$ vs T and $-(\partial \ln S / \partial P)_T$ vs T curves. These maxima shift towards

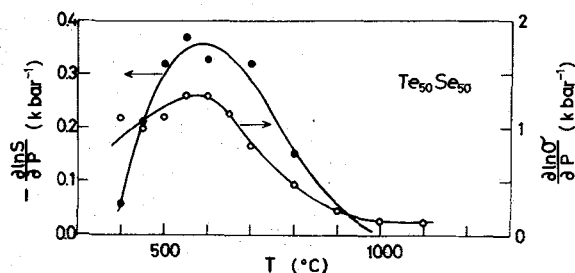


Fig. 2. The pressure coefficient of σ , $(\partial \ln \sigma / \partial P)_T$ (○), and that of S , $(\partial \ln S / \partial P)_T$ (●), as a function of temperature for liquid $\text{Te}_{50}\text{Se}_{50}$ mixtures.

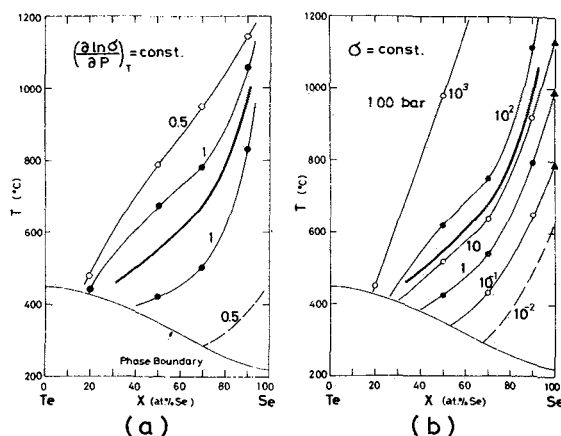


Fig. 3. (a) Contour of constant $(\partial \ln \sigma / \partial P)_T$ on the X-T plane. Numbers denote $(\partial \ln \sigma / \partial P)_T$ in kbar^{-1} . (b) Contour of constant σ on the X-T plane. Numbers denote σ in $\text{ohm}^{-1} \text{ cm}^{-1}$.

higher temperatures with Se concentration.

In Fig. 3 (a), the contours of constant $(\partial \ln \sigma / \partial P)_T$ are shown on the concentration X - temperature T plane. The bold line denotes the region where $(\partial \ln \sigma / \partial P)_T$ has the maximum value. The locus of the maximum of $-(\partial \ln S / \partial P)_T$ also falls nearly on the bold line in Fig. 3 (a). Figure 3 (b) shows the contours of constant σ on the X-T plane at 100 bar, together with the same bold line as in Fig. 3 (a).

A new result of S for liquid pure Se is

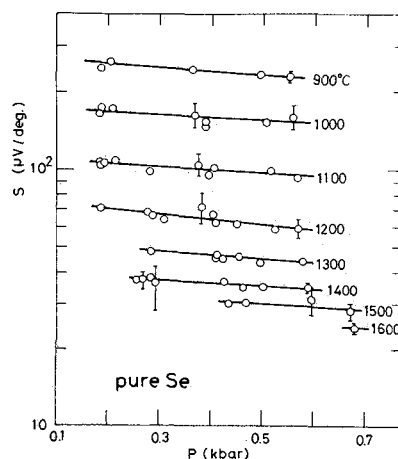


Fig. 4. Isotherms of S for liquid Se as a function of pressure.

presented in Fig. 4 as a function of pressure. The pressure and temperature variations of S obtained by us show nearly the same trend as those by Fischer and Schmutzler[4], though the absolute values of S by us are about 30 % smaller than those by them. The pressure coefficient of S is large around 1200°C , to which one attains when the bold line in Fig. 3 is extrapolated to 100 % Se.

Figure 5 shows the results of β_S for liquid Te-Se mixtures as a function of temperature, together with β_S for liquid pure Te [5] and Se [6]. At low temperatures the β_S - T curves for the mixtures show almost the same trend as that for pure Se. With raising temperature β_S -values of the mixtures increase more rapidly than those of Se and they have the maximum values at 440°C for liquid $\text{Te}_{70}\text{Se}_{30}$, at 610°C for $\text{Te}_{50}\text{Se}_{50}$ and at 750°C for $\text{Te}_{30}\text{Se}_{70}$. At higher temperatures β_S of the mixtures decreases with increasing temperature, which is the same behaviour as that of liquid pure Te. It is noticed that the region at which the maximum appears in

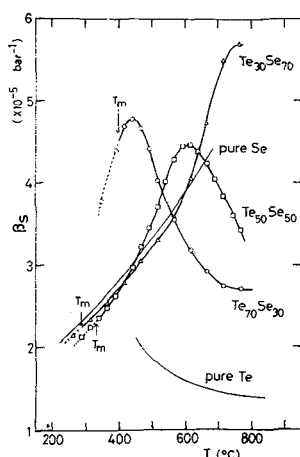


Fig. 5. Temperature variations of β_S for liquid Te-Se mixtures together with β_S for liquid pure Te 5 and Se 6 .

β_S coincides approximately with the bold line on the X-T plane in Fig. 3, where the semiconductor-to-metal transition are induced by a slight application of pressure.

Figure 6 shows the temperature variation of C for liquid $\text{Te}_{50}\text{Se}_{50}$ mixture. The sound velocity increases considerably with increasing pressure and the temperature at which C shows a minimum shifts towards lower temperatures with increasing pressure. This suggests that the temperature of the semiconductor-to-metal transition decreases with increasing pressure, which has been confirmed by the conductivity measurement under pressures.

As seen in Fig. 5, the large compressibility indicates that there exist large density fluctuations near the transition region. Near the region, there appears the anomaly in the molar volume V_m vs temperature curves (see Fig. 7 (a)), that is, the thermal expansion coefficient α_p changes from positive to negative[1]. Furthermore the concentration variations of other properties such as the Knight shift[7] and

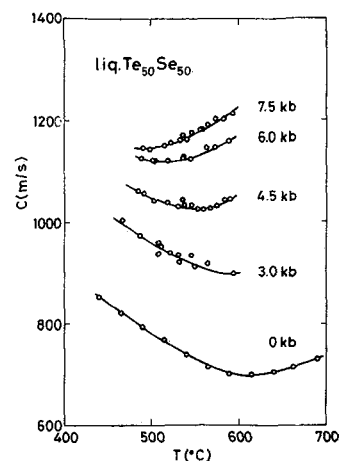


Fig. 6. Temperature variations of the sound velocity for liquid $\text{Te}_{50}\text{Se}_{50}$ at various pressures.

the average coordination number [8,9] exhibit anomalous behaviours in the same region.

The fact that the maximum in compressibility appears near the region where α_p changes from positive to negative can be interpreted by the sketches shown in Figs. 7 (a) and (b). These figures show the thermodynamic aspects of the structural transition from Se-like loosely packed atoms with twofold coordination to a Te-like densely packed structure with highly coordinated atoms in the mixtures. The sharp structural transition, which is indicated by the dashed lines in Figs. 7 (a) and (b), is smeared out owing to the thermal agitation.

As a final remark, we refer to the results of recent density and NMR measurements for liquid pure Se [10,11]. It was found that the isochores on the P-T plane have an inflection at high temperatures and that the pressure variation of the resonance shift due to the paramagnetic dangling bonds shows anomalous behaviours at high temperatures. These evidences may

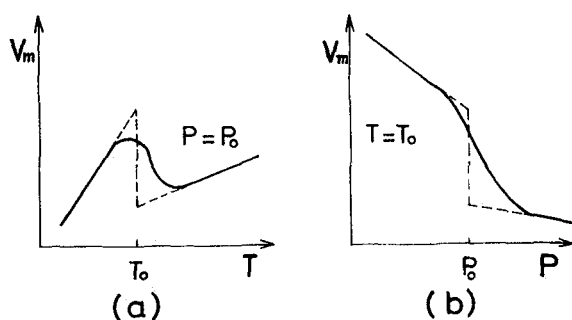


Fig. 7. (a) The solid line indicates the temperature variation of molar volume at constant pressure. (b) The solid line indicates the pressure variation of molar volume at constant temperature. The dashed lines indicate typical variations of V_m in the case of the first order phase transition.

suggest that a structural transition similar to that in liquid Te-Se mixtures occurs even in liquid pure Se.

ACKNOWLEDGEMENTS-- The authors wish to express their thanks to Dr. K. Tamura, Mr. M. Misonou and Mr. M. Mushiage for valuable discussions.

REFERENCES

1. Thurn, H and Ruska, J., *J. Non-Cryst. Solids* **22**, 331 (1976).
2. Yao, M., Misonou, M., Tamura, K., Ishida, K., Tsuji, K. and Endo, H., *J. Phys. Soc. Japan* **48**, 109 (1980).
3. Yao, M., Suzuki, K. and Endo, H., *Solid State Commun.* **34**, 187 (1980).
4. Fischer, R. and Schmutzler, R.W., *The Physics of Selenium and Tellurium*, ed. Gerlach, E. and Gross, P., 1979 (Springer, New York) P. 225.
5. Gitis, M.B. and Mikhailov, I.G., *Sov. Phys. Acoust.* **12**, 14 (1966).
6. Gitis, M.B. and Mikhailov, I.G., *Sov. Phys. Acoust.* **13**, 251 (1967).
7. Seymour, E.F. and Brown, D., *Proc. Int. Conf. Liquid Metals*, ed. Takeuchi, S., 1972 (Taylor and Francis) P. 399.
8. Hoyer, W., Thomas, E. and Wobst, M., *Z. Naturforschung*, **30a**, 1633 (1975).
9. Bellissent, R. and Tourand, G., *J. Non-Cryst. Solids* **35** and **36**, 1221 (1980).
10. Fischer, R., Schmutzler, R.W. and Hensel, F., *J. Non-Cryst. Solids* **35** and **36**, 1295 (1980).
11. Warren, Jr., W.W. and Duree, R., to be published.