Sound velocity of liquid se-te mixture

K. Takimoto[a]; H. Endo[a]

[a] Department of Physics, Faculty of Science, Kyoto University, Kyoto, Japan

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K. TAKIMOTO and H. ENDO

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

We have measured the sound velocity of liquid Se-Te mixtures up to 1050°C and 1500 bar, and estimated the adiabatic compressibility β_S and the long wavelength limit of density-density correlation function, $S_{NN}(0)$. There appear the maxima in the temperature variations of β_S and the inflections in those of $S_{NN}(0)$, which indicate clearly the transformation from Se-like to Te-like structure associated with pressure-induced semiconductor-to-metal transition.

INTRODUCTION

The difference in the electronic properties between liquid Se and liquid Te is related to the difference between their structures. In the liquid state Se shows semiconducting behaviour, and the chain structure is preserved.[1] On the other hand, liquid Te shows metallic behaviour, and the structure is believed to contain a large fraction of three-fold coordinated sites.[2] In liquid Se-Te mixtures, it is known that the transition from semiconducting to metallic nature occurs with raising temperature or increasing Te concentration.[3]

The X-ray diffraction experiment[4] indicates that the average coordination number of liquid Se-Te mixtures at 460°C remains nearly two irrespective of composition in the Se-rich region and it increases with Te concentration in the Te-rich region. From the density measurement,[5] it is found that at high temperatures the molar volume in the mixtures contracts by raising temperature and the region where the volume contraction occurs moves to lower temperature with increasing Te concentration. It is noticed that in such a region the conductivity shows a substantial increase by a slight application of pressure.[6] Recent measurements of magnetic susceptibility[7] and NMR[8] suggest that a sufficiently large number of dangling bond, C_1^0, due to bond breaking result in delocalization of the gap states. Delocalization

is accompanied by the collapse of the chain structure, which causes the transition from semiconductor to metal.

These results seem to show that the electronic transition in liquid Se-Te mixtures is correlated with the structural transformation. The measurements of the thermodynamic properties are considered to give valuable information to understand such a transformation. The measurement of sound velocity is one of the powerful ways.

In this paper we report the results for the sound velocity of liquid Se-Te mixtures under high temperature and high pressure, and discuss the thermodynamic properties such as the compressibility and the density fluctuations deduced from the sound velocity.

2   EXPERIMENTAL PROCEDURE

Figure 1 shows the cell assembly used for the measurement of the sound velocity in liquid Se-Te mixtures. Because of the corrosive nature of the specimen all the parts of the cell were made of sintered alumina. The specimen thickness in the test part was kept 3.00 mm by putting an alumina ring spacer between two alumina buffer rods in an alumina cylinder. One of the buffer rods was 100 mm in axial length and the other 110 mm, and both were 11.3 mm in diameter. A pair of quartz transducer A and B of 20 MHz were bonded to the cold ends of buffer rods, which were attached to copper blocks in contact with the inner wall of the high pressure vessel. The specimen in the test part was heated up by Mo heater and the specimen in the reservoir by nichrome heater. The temperature of the test part and reservoir were measured by alumel:chromel thermocouples attached to the outer walls of the alumina cylinder and reservoir.
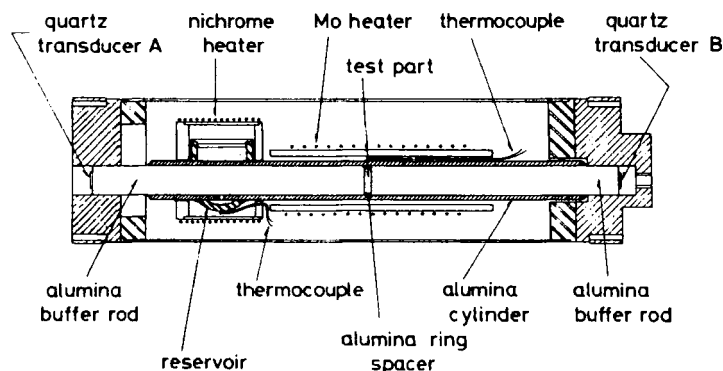

FIGURE 1   Cell assembly.

The cell was set in the high pressure vessel (60 mm in inner diameter) made of high-strength steel (SNCM8). Ar gas was used as pressure transmitting medium. The pressure was measured by a Heise gauge with an accuracy ± 5 bar. Alumina powder was filled in the high temperature zone in order to obtain good thermal insulation and to suppress the convection of Ar gas.

The introduction of liquid specimen into the test part is as follows. The entire assembly was evacuated and the test part was heated up to a temperature above the melting point of the specimen. Then the reservoir loaded with the solid specimen was heated to melt the specimen. Finally Ar gas was let into the pressure vessel to push the liquid specimen into the test part through the narrow interstice between the alumina cylinder and the alumina buffer rods.

The sound velocity measurements were carried out by the ultrasonic pulse transmission/echo technique.[9] First, the time required for an ultrasonic pulse to traverse from transducer A to transducer B was measured. Then the time required for an echo to return from the rod/specimen interface to the transducer was measured for each buffer rods. The time required for a pulse to traverse the specimen was the difference between the time required for a pulse to travel from transducer A to transducer B and the average of above two echo-times. The sound velocity was calculated from the specimen thickness and the specimen traverse time. The experimental errors in the sound velocity and temperature were within 2% and $\pm 10°C$.

3 RESULTS

Figure 2 shows the temperature variation of the sound velocity v_s at atmospheric pressure for liquid Se-Te mixtures with various Te concentration together with the data for pure liquid Te by Gitis et al.[10] For liquid Se a substantial decrease of v_s is observed by raising temperature. The value of v_s at 600°C is 815 m/sec, smaller by 30% than at the melting point. The temperature variation of v_s for liquid mixtures shows a minimum. The temperature where v_s shows a minimum, T_{min}, is 490°C for $Se_{30}Te_{70}$, 545°C for $Se_{40}Te_{60}$, and 680°C for $Se_{50}Te_{50}$. For liquid $Se_{60}Te_{40}$, v_s seems to have a minimum value around 780°C. It is noticed that at low temperatures the temperature dependence of v_s for liquid mixtures is similar to that for liquid Se and at high temperatures is similar to that for liquid Te. With increasing Se concentration, T_{min} shifts towards higher temperature. Figure 3 shows temperature variation of v_s for liquid Se-Te mixtures at 500 bar, which is similar to that at atmospheric pressure. The temperature variation of v_s for the mixtures shows minimum at 730°C for $Se_{60}Te_{40}$, at 665°C for $Se_{50}T_{50}$, at 550°C for $Se_{40}Te_{60}$, and at 500°C for $Se_{30}Te_{70}$.

FIGURE 2 Temperature variation of the sound velocity v_s for Se-Te mixtures at atmospheric pressure. The result of v_s for pure liquid Te[10] is shown for reference.
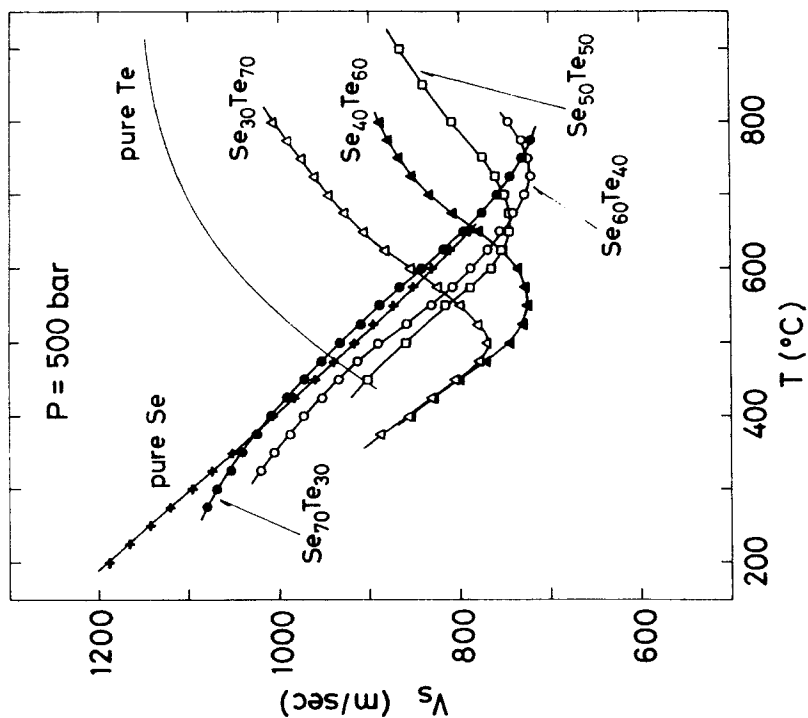
FIGURE 3 Temperature variation of the sound velocity v_s for Se-Te mixtures at 500 bar. The result of v_s for pure liquid Te at atmospheric pressure[10] is shown for reference.
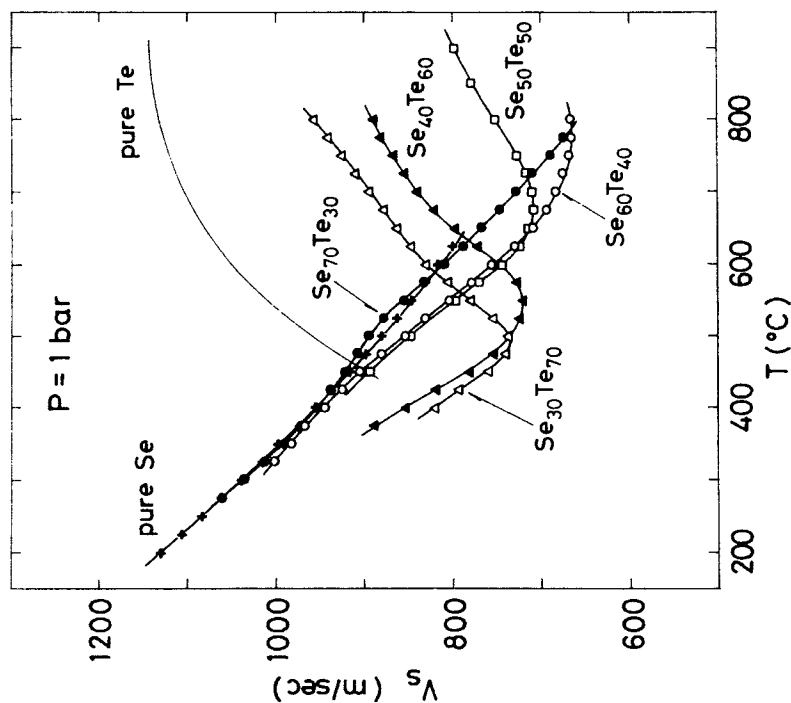
FIGURE 5 Temperature variation of the sound velocity v_s for liquid $Se_{50}Te_{50}$ under various pressure. The results of v_s for pure liquid Se and Te[10] at atmospheric pressure are shown for reference.
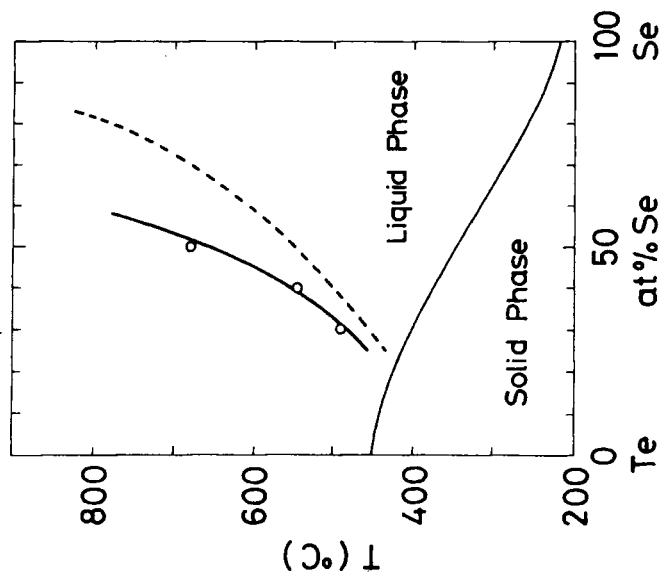

FIGURE 4 T_{min} at atmospheric pressure shown on the concentration x and temperature T plane. The dashed line shows the region at which the pressure-induced semiconductor-to-metal transition occurs.[6]
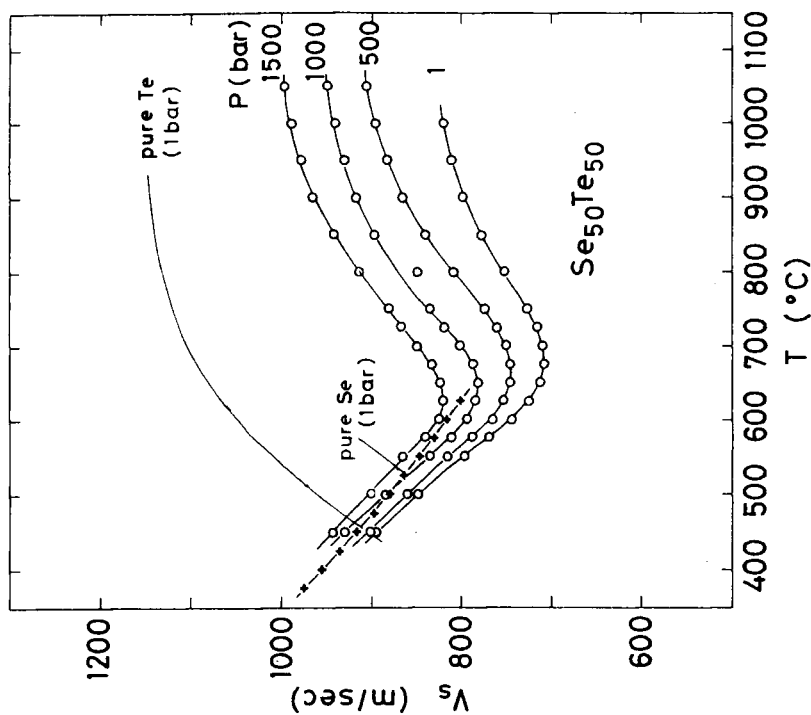
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Figure 4 shows T_{min} at atmospheric pressure as a function of Se concentration. As seen in the figure, T_{min} increases rapidly with increasing Se concentration. The dashed line in the figure denotes the region at which the pressure-induced semiconductor-to-metal transition occurs.[6] The region at which v_s has a minimum lies closely to the dashed line, though the latter locates at lower temperatures than the former.

Figure 5 shows the temperature variation of v_s for $Se_{50}Te_{50}$ under various pressures, together with the data for liquid Se and Te[10] at atmospheric pressure. At low temperatures the temperature variation of v_s is similar to that of liquid Se and at high temperatures to that of liquid Te. By application of pressure v_s increases. The pressure variation of v_s at high temperatures is large compared with that at low temperatures. At sufficiently high pressures, the value of v_s at high temperatures is likely to approach to that of liquid Te at atmospheric pressure. It is noticed that the minimum in the v_s-T curves becomes sharp with increasing pressure.
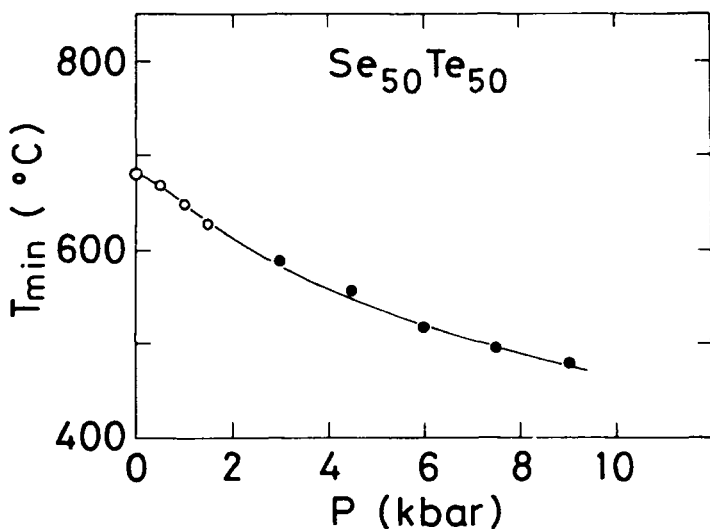
FIGURE 6 Pressure variation of T_{min} for liquid $Se_{50}Te_{50}$. The high pressure data are taken from the results by Mushiage et al.[11]

In Figure 6, T_{min} is plotted as a function of pressure. The high pressure data in the figure are taken from the results by Mushiage et al.[11] using piston-cylinder high pressure apparatus. Our data points can be joined to the data at higher pressures by a smooth line. By a slight application of pressure T_{min} decreases substantially.

4   DISCUSSION

The adiabatic compressibility β_S can be deduced from the measured sound velocity using the following relation;

$$\beta_S = \frac{1}{\rho v_s^2}, \tag{1}$$

where ρ is the density. Figure 7 shows β_S obtained for liquid Se-Te mixtures at atmospheric pressure. The value of the density were taken from the data
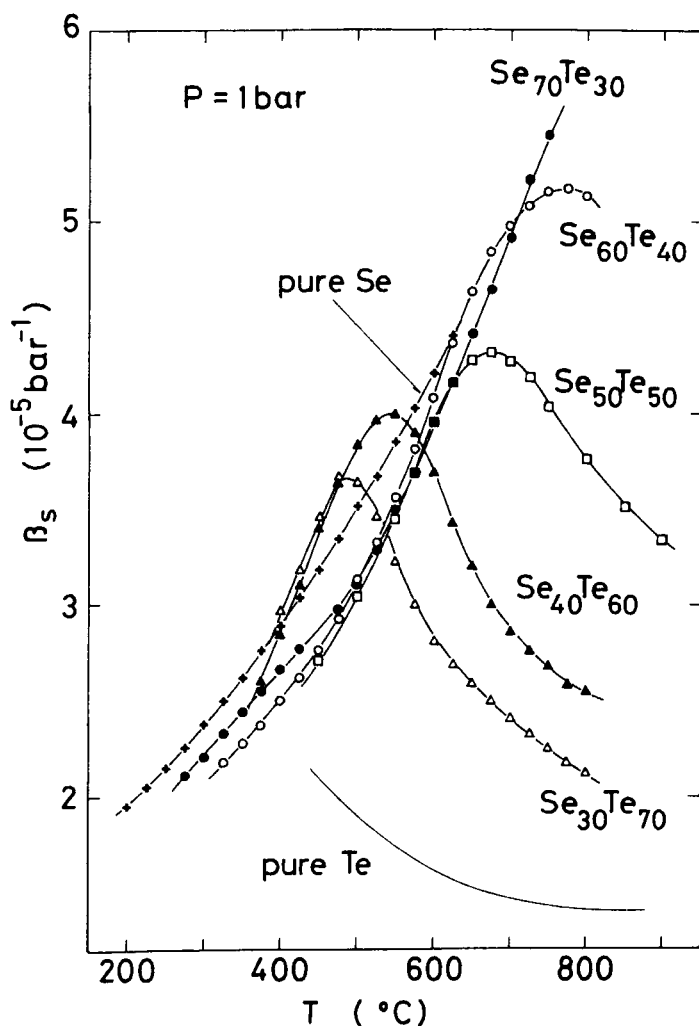

FIGURE 7   Adiabatic compressibility β_s for liquid Se-Te mixtures at atmospheric pressure.

by Thurn and Ruska.[5] With increasing temperature, β_S increases remarkably and decreases through the maximum. Although the maximum in β_S was not observed in Se-rich concentration range on the present experimental condition, there seems to appear the maximum at a very high temperature. The peak height of β_S decreases and the peak position moves to lower temperature with increasing Te concentration. It should be pointed out that the thermal expansion coefficient α_p is zero near the region where the maximum in β_S appears. When $\alpha_p = 0$, the specific heat ratio γ is unity and hence β_S is equal to the isothermal compressibility β_T. The temperature variation of β_S of the liquid mixtures at low temperatures is similar to that of pure liquid Se and at high temperatures to that of pure liquid Te. The maximum in β_S is associated with the structural transition from Se-like loosely packed to Te-like densely packed structure. It is noticed that the width of the peak of β_S curve becomes narrower with increasing Te concentration.

The long wavelength limit of the density-density correlation function, $S_{NN}(0)$, which is a measure of the density fluctuations in the liquid mixture is given as follows;

$$S_{NN}(0) = nk_BT\beta_T + \delta^2 S_{CC}(0), \qquad (2)$$

where n is the number density, β_T the isothermal compressibility, $S_{CC}(0)$ the long wavelength limit of the concentration-concentration correlation function, and δ the dilatation factor defined by

$$\delta = \frac{V_1 - V_2}{cV_1 + (1 - c)V_2}. \qquad (3)$$

Here V_1 and V_2 are the partial molar volumes and c is the concentration of species 1. Figure 8 shows $S_{NN}(0)$, which is estimated from the equation (2) assuming that $\gamma = 1$ ($\beta_T = \beta_S$). The contribution of the second term in the equation (2) to $S_{NN}(0)$ is small compared with the first term, unless the concentration fluctuations are sufficiently large.

A remarkable increase of $S_{NN}(0)$ is seen for liquid Se when the temperature is raised. At low temperatures the $S_{NN}(0)$-T curve for liquid mixtures nearly falls on that for liquid Se. At high temperatures $S_{NN}(0)$ of the mixtures turn to decrease and the temperature range at which the rapid decrease in $S_{NN}(0)$ is observed becomes narrower with increasing Te concentration. At sufficiently high temperatures, the temperature variation of $S_{NN}(0)$ becomes similar to that for liquid Te.

In the liquid Se-Te mixtures Se atoms in polymer chains are considered to be substituted by Te atoms. A rapid increase in $S_{NN}(0)$ at low temperatures may arise from the thermal fluctuations of the distance between polymer chains. The inflection in $S_{NN}(0)$ at high temperatures is related to the collapse of the chain structure. From the NMR measurement, Misonou and Endo[8]
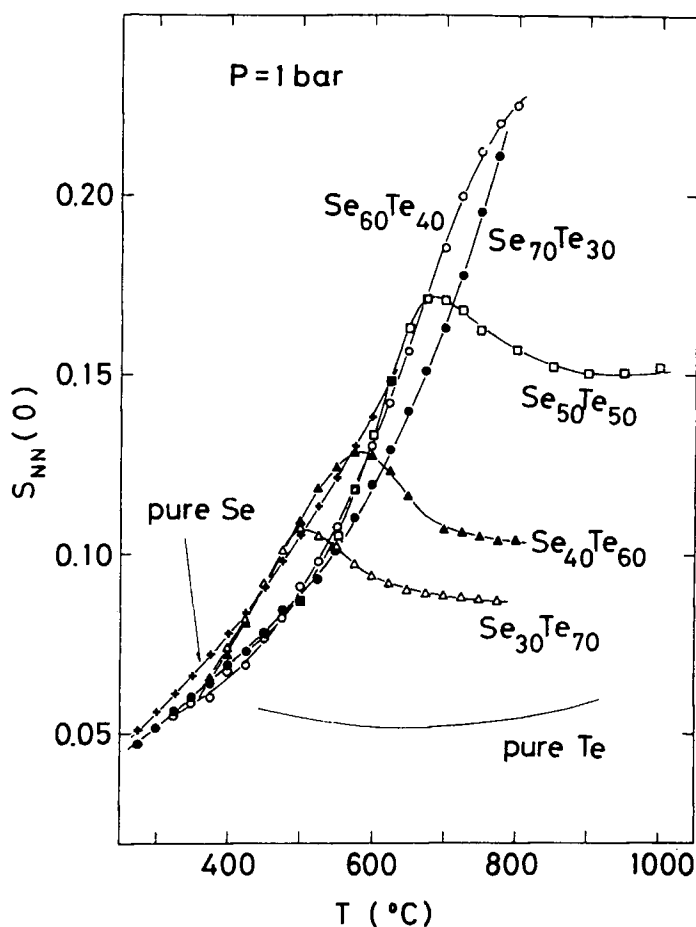
FIGURE 8   Long wavelength limit of density-density correlation function, $S_{NN}(0)$, for liquid Se-Te mixtures at atmospheric pressure.

suggested that the environment around Te sites rather than Se sites changes when the chain structure collapses. The rapid decrease in $S_{NN}(0)$ implies that twofold coordinated Te is transformed to threefold coordinated state. Such a collapse of chain structure will be accelerated with increasing Te concentration. This is the reason why the temperature range at which the rapid decrease in $S_{NN}(0)$ is observed becomes narrower with increasing Te concentration. As seen in Figure 8, $S_{NN}(0)$ depends weakly upon the temperature at high temperatures, where twofold coordinated and threefold coordinated sites coexist.

The substitutions of Se atoms in the polymer chains by Te atoms result in the weakening of bond strength in the chains. The energy gap between the valence and conduction bands becomes narrow and the bonds tend to be easily broken. A number of dangling bond states C_1^0 produced by the bond breaking will introduce a narrow band in the centre of the gap. The number of C_1^0 states increases with increasing Te concentration, and the gap states are expected to be delocalized. Delocalization is a consequence of the collapse of the chain structure around Te sites in which localized C_1^0 states are destroyed in favour of delocalized threefold coordinated states, C_3^0. Therefore the temperature at which the structural transition occurs moves to lower temperature with increasing Te concentration. This is reflected on the behaviour of $S_{NN}(0)$ shown in Figure 8. The inflection in the $S_{NN}(0)$-T curve moves to higher temperature with increasing Se concentration. We may expect that such an inflection in $S_{NN}(0)$-T curve appears in pure liquid Se at a very high temperature and probably under pressure. Large thermal fluctuations in the chain distance and the resulting large number of C_1^0 states are required for the collapse of chain structure of Se, because the bond strength is strong and the band gap is large in liquid Se compared with the liquid mixtures.

Acknowledgement

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