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Thermodynamic evidence for a structural transition of liquid Te in the supercooled region

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Abstract. The specific heat, thermal expansion coefficient and compressibility of liquid Te have been measured to investigate the structural transition expected in the supercooled state. All these thermodynamic functions have extrema at $353 \pm 3^\circ\text{C}$, a fact which provides clear evidence for the structural change of Te to the twofold liquid in the supercooled region. It is shown that Ehrenfest's relations are satisfied among the excess specific heat, isothermal compressibility and thermal expansion coefficient associated with the structural change.

1. Introduction

The structural evolution of liquid tellurium (Te) with increasing temperature has been a long standing problem (Cabane and Friedel 1971, Enderby and Gay 1980, Menelle *et al* 1987, 1989). It is generally accepted that the gradual semimetal–metal transition of liquid Te is closely related to this structural change. In conjunction with similar electrical and structural transitions, various structural and thermodynamic investigations from both experimental and theoretical viewpoints have been carried out in order to clarify the structural evolution in a liquid Se–Te alloy. A Se-rich alloy at low temperatures has a structure characterized by twofold coordination (referred to as a L-form) and it transforms with temperature, pressure and increasing Te concentration to a high temperature (H) form specified by threefold atoms and a random network structure (Bellissent and Tourand 1981, Misawa and Suzuki 1980), although the consensus of opinion seems to be against the latter structure. In the transitional region between the two forms, the thermal expansion coefficient, α_p , the isothermal compressibility, κ_T , and the constant pressure specific heat, C_p , show extrema (Thurn and Ruska 1976, Takimoto and Endo 1982, Tsuchiya 1988a, 1991, Takeda *et al* 1987, Kakinuma and Ohno 1987). It has been shown using a kind of two-state model, referred to as an inhomogeneous structure model (abbreviated as IHSM), that the anomalous behaviour of these thermodynamic functions is brought about by a structural change in the liquid (Tsuchiya and Seymour 1982, 1985, Tsuchiya 1986). Evidence has been presented that the Ehrenfest relations for the second kind of phase transition are satisfied among the temperature dependencies of α_p , κ_T and C_p . In general, however, a phase transition is blurred by alloying due to unavoidable concentration fluctuations. For Se–Te alloys the peak width of these thermodynamic functions is broadened with increasing Se concentration. Thus

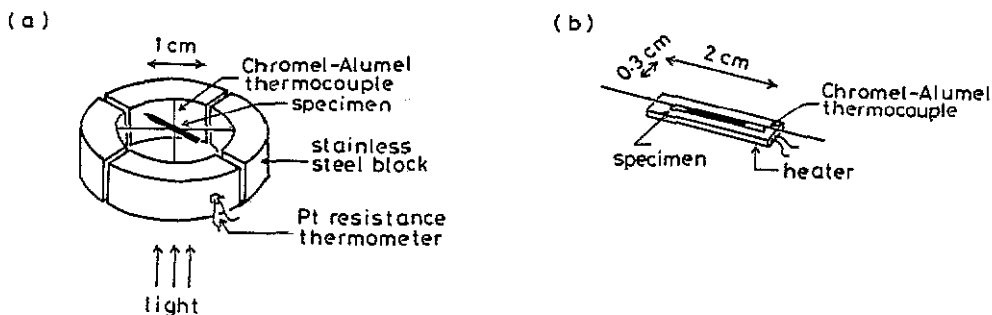


Figure 1. Schematic drawing of the specimen and thermocouple arrangement for (a) the AC calorimetry, and (b) the volume measurements. The light from below heats the specimen intermittently.

it is desirable to investigate Te in detail for better understanding of a structural transition of this kind.

Liquid Te at the melting point is believed to be at the lower boundary of the η -form, and the thermodynamic anomaly around the melting point has been interpreted based on a tacit assumption that liquid Te would transform in the supercooled state to a liquid with a chain structure similar to that of liquid Se. If this is the case, the extrema in the thermodynamic functions would appear around 350 °C as observed for the alloys with moderate Se concentration (Tsuchiya and Seymour 1985). Unfortunately, since the lowest supercooled temperature of bulk liquid Te is around 370 °C, available thermodynamic data are mostly for the temperatures above the melting point, and such extrema have not been confirmed yet.

It is well known that the freezing point can be substantially lowered from the normal melting point by keeping a uniform temperature over a small specimen. In this paper AC calorimetry (Sullivan and Seidel 1968) has been applied to Te with a volume of about $5 \times 10^{-4} \text{ cm}^3$ ($\sim 3 \times 10^{-3} \text{ g}$) to measure the specific heat of supercooled Te. The temperature dependence of the volume has also been measured on a specimen with a similar size. The lowest supercooled temperature attained was 280 °C. In addition, the sound velocity was measured down to 333 °C to compliment the previous data (Tsuchiya 1988b). Marked peaks in C_p , α_p and κ_T have been clearly observed at $353 \pm 3 \text{ °C}$. We discuss the nature of the structural transition, and recent experimental and theoretical studies of the structure of liquid Te.

2. Experiment

The arrangement of a specimen and a thermocouple for AC specific heat measurements is schematically shown in figure 1(a). Te was sealed in a capillary tube made of fused silica of which the outer and inner diameters were 0.40 and 0.34 mm, respectively. The outer surface of the capillary tube was painted with colloidal carbon. The length of Te was about 0.6 cm. The specimen and chromel-alumel thermocouples of 0.025 mm diameter were stuck together with silver paste. The thermocouple ends were connected to four stainless steel blocks of which the temperature was measured with a calibrated Pt resistance thermometer. One of the thermocouples measures the temperature difference between the specimen and the block and the other picks up the AC component of the temperature. The apparatus was ACC-1 of Shinku-Riko Co Ltd which uses chopped

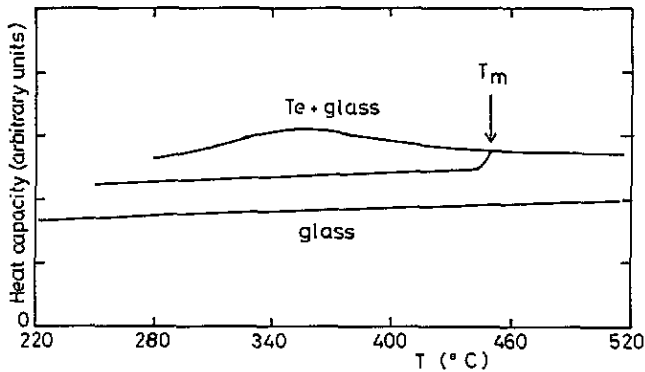


Figure 2. The AC calorimeter output trace for Te and glass. The upper branch for Te is for the liquid and the lower one is for the solid. T_m denotes the melting point.

light as an AC heat source. Several AC frequencies between 1 and 4 Hz were used to ensure that the results were not affected by the thermal diffusivity of the specimen. After measurements the tip of the capillary was clipped, and Te was distilled out of the capillary. The clipped glass tip was less than 0.05% of the total. The empty capillary was then measured with the same arrangement, described above.

The arrangement of a specimen and a thermocouple for volume measurements is schematically shown in figure 1(b). The specimen was made using the same method as that used for the specific heat measurements. Care was taken so that no void was contained in the specimen. The specimen and a chromel–alumel thermocouple were stuck together on a small plate heater using silver paste. The whole arrangement was put into a transparent fused silica dewar. The temperature was controlled, using a digital temperature controller, to within 0.5 °C. The length of Te, typically 0.8 cm, was measured with a travelling microscope measurable to 2×10^{-5} cm. The thermocouple was calibrated by observing the melting point of Te which was taken as 450 °C (Iida and Guthrie 1988). Measurements were restricted below 600 °C because the menisci of Te were not stable due to rapid evaporation.

The sound velocity, v_s , has been measured with a conventional pulse technique to complement the results reported previously. Since a large specimen had to be used, the lowest supercooled temperature was 333 °C. Details of the measurements were the same as reported elsewhere (Tsuchiya 1988b).

3. Results and analysis

3.1. Specific heat

The output trace of the calorimeter is plotted in figure 2, and it is proportional to the composite heat capacity of Te, glass, thermocouples, and silver paste. At the melting point of Te, the output jumps discontinuously, corresponding to the difference in the specific heat of Te in the solid and liquid states. In the supercooled region, the output increases with decreasing temperature and goes through a maximum around 353 °C. No hysteresis was observed when the temperature was raised before solidification took place. The lowest supercooled temperature was 280 °C. In the present experiments, the amount of Te was too small to determine the mass to within 20% accuracy, so that the

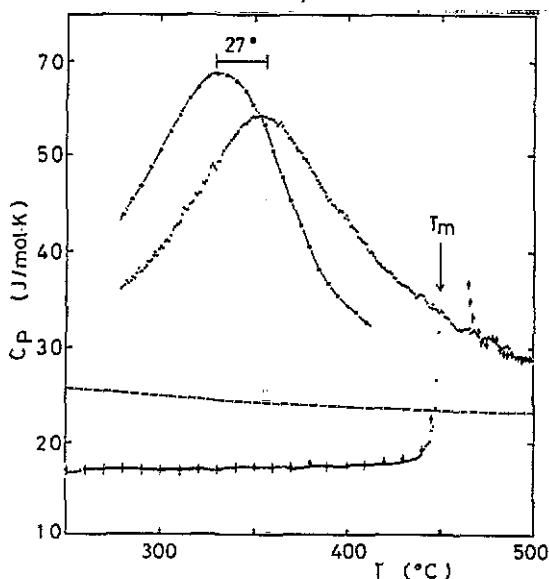


Figure 3. The constant specific heat, C_p , for Te in the supercooled region. The data with error bars have been taken from Kakinuma and Ohno (1987, and a private communication). The latter for the solid almost coincide with the present results on this scale. The broken curve is C_p for liquid Se taken from Gaur *et al.* (1981). C_p at $1 \times 10^8 \text{ N m}^{-2}$ estimated from a thermodynamic relation described in the text is also plotted (chain curve).

output was converted to the specific heat using the following procedure. First, the output for the empty capillary was subtracted, then the net output for the solid was scaled up using the data for the solid Te in the overlapping temperature region (Medzhidov and Rasulov 1975). Although the specific heat determined in this way is dependent on the results for solid Te, the uncertainty of the present results will be within 5%, including the reproducibility of the present experiments. The specific heat obtained in this way has been plotted in figure 3. The results are in good agreement with those reported by Kakinuma and Ohno (1987 and in a private communication) measured using adiabatic scanning calorimetry in the overlapping temperature range. The specific heat increases with decreasing temperature in the supercooled region and takes a maximum at $353 \pm 3 \text{ }^\circ\text{C}$; the maximum value is $64.0 \pm 1 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.2. Molar volume

Since the mass of Te could not be determined, the observed length of Te in the capillary as a function of temperature was fitted to the molar volume determined using the γ -ray attenuation method (Tsuchiya 1988a). The results are plotted in figure 4 together with those reported previously. The uncertainty is estimated to be within 0.3%. The volume increases quite steeply with decreasing temperature around $350 \text{ }^\circ\text{C}$ and levels off below $300 \text{ }^\circ\text{C}$. All the data were fitted to equation (9) in section 4 from which the thermal expansion coefficient was evaluated using the relation $\alpha_p = (1/V)(\partial V/\partial T)_p$. The thermal expansion coefficient is also plotted in figure 4; it has a sharp negative peak around the temperature where the specific heat takes a maximum.

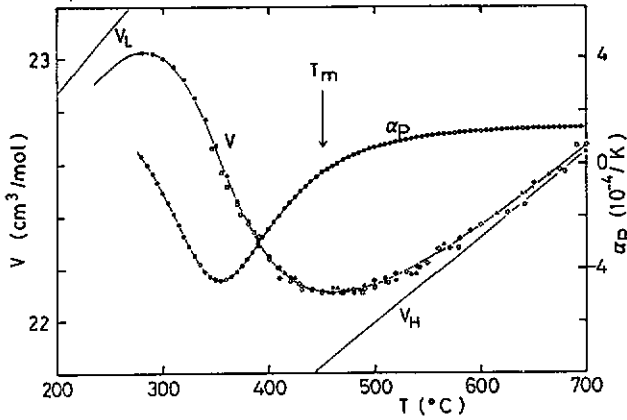


Figure 4. The molar volume, V , and thermal expansion coefficient, α_p , for liquid Te. The reference data have been taken from Tsuchiya (1988a) ($-\diamond-\diamond-$), Thurn and Ruska (1976) ($-\triangle-\triangle-$), and Ioffe and Regel (1960) ($-\square-\square-$). The curve through the data is the prediction of equation (9). Straight lines are for V_L and V_H described in the text.

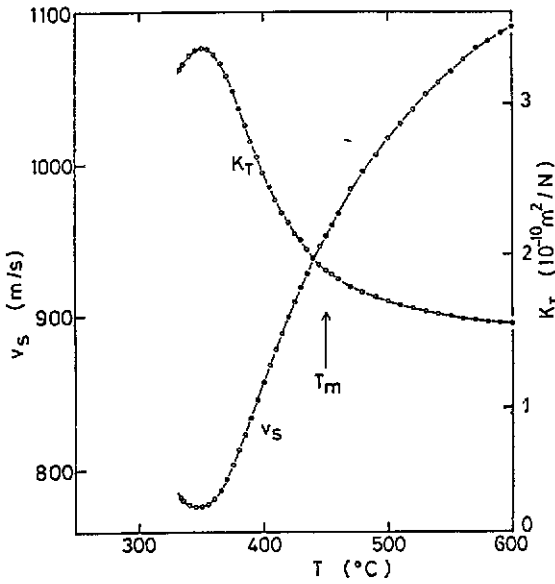


Figure 5. The velocity of sound, v_s , and isothermal compressibility, κ_T , for Te in the supercooled region.

3.3. Isothermal compressibility

As reported previously (Tsuchiya 1988b), the sound velocity, v_s , decreases quite steeply in the supercooled region. In the present experiment the supercooled region was extended to 333 °C and a minimum was confirmed as shown in figure 5. The isothermal compressibility may be evaluated from the relation $\kappa_T = 1/\rho v_s^2 + TV\alpha_p^2/C_p$ where ρ is the mass density. The results are plotted in figure 5. Overall uncertainty was estimated to within 0.7%.

4. Discussion

The stability of a supercooled liquid is usually discussed in terms of the nucleation probability of critical size crystalline embryos. The latter depends on such factors as the enthalpy and entropy of fusion and the interfacial energy of the crystal and melts (see, for example, Shimoji 1977). No satisfactory theory appears to have been presented to account for the stability of the supercooled liquids for a given material; nevertheless it is empirically well known that an element having a large melting entropy, such as Ga or Bi, has the wide range of a metastable supercooled liquid, and Te belongs to this category as well. Although subdividing a liquid metal into many small independent volumes is very effective for lowering the supercool temperature substantially, the lowest attainable temperature is a function of the experimental conditions imposed. In the present experiment, the supercooled region could be extended down to 280 °C for the specific heat and volume measurements, and 333 °C for the sound velocity measurements. In the former experiments the vertical temperature gradient would be very small due to the small diameter of the specimen and the geometrical arrangement shown in figure 1; then the convection of the liquid would be greatly diminished. Moreover, there was no mechanical disturbance despite the fact that continuous vibration has to be applied to a specimen for the latter measurements. These factors would explain the discrepancy of the lowest temperatures in the different experiments.

The rising value of C_p with increasing supercooling is a common feature of liquid metals (Perepezko and Paik 1984); however, no other metals show a prominent peak in C_p like that shown by Te. When Se and S are added, the peak position shifts towards the higher temperatures while the melting point is lowered and the peak appears well above the liquidus line (Kakinuma and Ohno 1988). The thermal expansion coefficient and the isothermal compressibility show similar behaviour (Thurn and Ruska 1976, Tsuchiya 1988a, 1991). Then, it may be difficult to interpret the present results as being due to the nucleation or fluctuations of a crystalline phase.

In relation to the semiconductor–metal transition of liquid Se–Te alloys, a microscopic model for the thermodynamic transition has been developed by Cutler and his co-workers (Cutler and Rasolondramanitra 1985, Cutler *et al* 1990). They have proposed that thermally excited bond defects in the chain molecules of neutral chalcogen atoms, referred to as D_p centres consisting of a threefold D^+ atom coupled with a onefold D^- ion, play an essential role in the thermodynamic transition. They have introduced the idea that the electrostriction associated with D^- ions causes the local volume contraction and an apparent increase of coordination number in the transitional temperature region. However, factors determining the equilibrium concentration of bond defects based on the microscopic model are still far from fully understood and the mutual relations among the temperature dependences of α_p , C_p and κ_T remain unresolved.

As mentioned in section 1, on the other hand, it has been shown that the structural transition in the Se–Te system conforms to the Gibbs free energy having a functional form, $G(T, P, C)$, where C denotes the fraction of atoms in a H -form (Tsuchiya 1988a, 1990). In the transitional temperature region ($0 < C < 1$), the thermodynamic parameters take the following forms:

$$C_p = C_p^0 + \delta C_p \quad (1)$$

$$\alpha_p = \alpha_p^0 + \delta \alpha_p \quad (2)$$

$$\kappa_T = \kappa_T^0 + \delta \kappa_T \quad (3)$$

where the first term of the right-hand side is a thermodynamic parameter expected

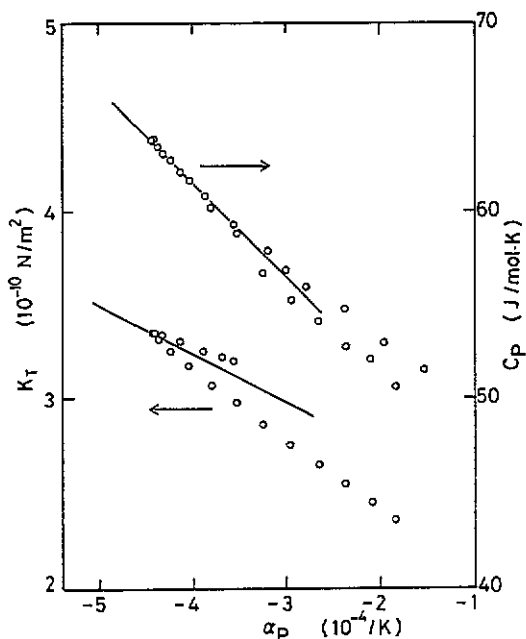


Figure 6. Dependences on the thermal expansion coefficient, α_p , of the constant pressure specific heat, C_p , and the isothermal compressibility, κ_T . Apparently the predictions for the Ehrenfest relations are borne out.

assuming no structural change, and the second is the excess part associated with the rate of change of the fraction of H-form Te, C , with temperature or pressure. The excess terms are not all independent of one another, but satisfy the following relations:

$$\delta C_p / \delta \alpha_p = TV(\partial P / \partial T)_C \quad (4)$$

$$\delta \kappa_T / \delta \alpha_p = (\partial T / \partial P)_C \quad (5)$$

$$(1/TV)\delta C_p \delta \kappa_T / \delta \alpha_p^2 = 1. \quad (6)$$

These relations are formally equivalent to the Ehrenfest relations for the second kind of phase transition and the left-hand side of equation (6) is called the Prigogine-Defay ratio. Here $(\partial T / \partial P)_C$ is a constant C slope in the T - P plane.

To see that those relations are really satisfied for the structural transition in supercooled Te, the temperature dependences of the first terms of equations (1)–(3) have to be examined. At high temperatures where there is no longer structural change, the thermodynamic functions have only weak temperature dependences as is the normal behaviour of a liquid metal. On the other hand, at low temperatures where liquid Te is almost in the L-form they approach the temperature dependences extrapolated from the high temperature values, and their anomalous variation occurs only in the transitional region where the coordination number changes rapidly. Similar behaviour of the thermodynamic functions has been observed for the liquid Se-Te alloy as well. Then it is reasonable to assume that the second terms dominate the whole temperature variation and C_p^0 , α_p^0 and κ_T^0 have weak temperature dependences as compared with the second terms. Then it would be expected from equations (4) and (5) that a plot of C_p or κ_T against α_p for various temperatures would result in a straight line with a slope given by $TV(\partial P / \partial T)_C$ or $(\partial T / \partial P)_C$. In figure 6, C_p and κ_T have been plotted against α_p where the temperature is an implicit variable. The slopes, determined by fitting the data between 330 and 380 °C to a linear relation, are $-(5.1 \pm 0.6) \times 10^4 \text{ J mol}^{-1}$ and $-(2.7 \pm 0.8) \times 10^{-7} \text{ K m}^2 \text{ N}^{-1}$, respectively, for C_p - α_p and κ_T - α_p plots. Large uncer-

tainty in the latter plot is due to duplex values of κ_T which may be mainly due to a non-linear temperature dependence of κ_T^0 , as discussed in a previous paper (Tsuchiya 1990). From these numerical figures, the Prigogine-Defay ratio is found to be 1.0 ± 0.4 .

The constant C slope in the T - P plane predicts that the peak position of a thermodynamic parameter shifts towards the lower temperatures at the rate $(\partial T/\partial P)_C = -2.7 \times 10^{-7} \text{ K m}^2 \text{ N}^{-1}$. Using a thermodynamic relation $(\partial C_p/\partial P)_T = -TV[\alpha_p^2 + (\partial \alpha_p/\partial T)_p]$, on the other hand, the pressure dependence of C_p may be evaluated. The specific heat at $1.0 \times 10^8 \text{ N m}^{-2}$ estimated using the relation has been plotted in figure 3. The peak in the C_p - T curve shifts with an applied pressure towards the lower temperatures by an amount evaluated from the slope shown in figure 6. Since no adjustable parameter is involved in the analysis, the overall consistency of the results suggests that the Ehrenfest relations are satisfied for the thermodynamic parameters associated with the structural transition of liquid Te.

Let us now consider a specific model to estimate the fraction of H-form Te. In a series of papers, the present author and Seymour have presented IHSM where the following Gibbs free energy, G , has been proposed to account for the thermodynamic properties associated with the structural transition in liquid Te (Tsuchiya and Seymour 1982, 1985):

$$G = CG_H + (1 - C)G_L + (RT/m)[C \ln C + (1 - C) \ln(1 - C)] + (\varepsilon_\Omega/m)C(1 - C) \quad (7)$$

where subscripts H and L refer respectively to H- and L-forms of Te. It is assumed that a group of m atoms change their local structure co-operatively. R is the gas constant and ε_Ω the interaction parameter between different forms of atom groups. The fraction of H-form Te, C , is given by the stability condition $(\partial G/\partial C)_{T,P} = 0$,

$$\ln C/(1 - C) = -[m\Delta G + (1 - C)\varepsilon_\Omega]/RT \quad (8)$$

where Δ refers to a difference in the corresponding thermodynamic quantities for H- and L-form Te. The molar volume and the enthalpy are derived using thermodynamic relations, $(\partial G/\partial P)_T$ and $G - T(\partial G/\partial T)_P$, and take the following forms,

$$V = CV_H + (1 - C)V_L \quad (9)$$

$$H = CH_H + (1 - C)H_L \quad (10)$$

The expressions for C_p , α_p and κ_T can be readily obtained from equations (9) and (10) and take the forms indicated by equations (1)–(3) (Tsuchiya and Seymour 1985). Assuming that V_H and V_L increase linearly with increasing temperature as is the normal behaviour of the volume for a liquid, the temperature dependence of the fraction of H-form Te can be evaluated from the temperature dependence of the molar volume in terms of $m\Delta G (=m\Delta H + m\Delta S)$ and ε_Ω where ΔH and ΔS are a transition enthalpy and a transition entropy for the L- to H-form transition in Te. Fitting the all data up to 950 °C to equation (9) together with equation (8), these parameters have been obtained as $m\Delta H = 68.27 \text{ kJ}$, $m\Delta S = 108.46 \text{ J K}$ and $\varepsilon_\Omega = 2.49 \text{ kJ}$. V_H and V_L are

$$V_H = 19.458 + 0.3276 \times 10^{-2} T \quad (\text{cm}^3 \text{ mol}^{-1})$$

$$V_L = 19.924 + 0.5944 \times 10^{-2} T \quad (\text{cm}^3 \text{ mol}^{-1}).$$

These parameters are in reasonable agreement with those evaluated previously where the analysis was based on the NMR Knight shift data above 400 °C (Tsuchiya and Seymour 1985). As shown by a smooth curve in figure 3, the results can satisfactorily reproduce the temperature dependence of the volume. In the framework of IHSM, the constant C

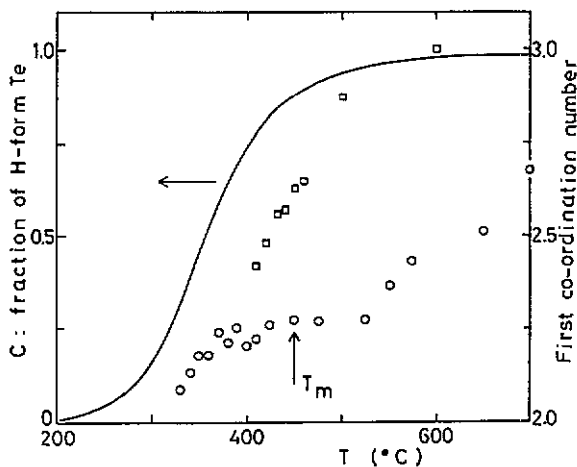


Figure 7. Dependences on temperature of C : the fraction of H-form Te, and the coordination number in the supercooled region. The latter has been taken from Menelle *et al* (1987) (—○—○—) and (1989) (—□—□—). The results for the coordination number appear to be contradicted; however, these researchers used different methods in each of the two reports to estimate the coordination number.

slope in the temperature–pressure plane is given by $(\partial P/\partial T)_C = T\Delta V/\Delta H$ (Tsuchiya and Seymour 1985) from which the transition enthalpy may be estimated. Using the slope of the C_p – α_p plot and ΔV around 350 °C, ΔH is obtained to be 4.7 kJ mol⁻¹. On the other hand, the transition enthalpy is related to the excess specific heat by $\delta C_p = \Delta H(\partial C/\partial T)_p$. Thus the area under δC_p corresponds to ΔH . For a rough estimation, we take the specific heat for Se (Gaur *et al* 1981) to be C_p^0 and assume that the excess specific heat, δC_p , is given by $C_p(\text{Te}) - C_p(\text{Se})$. The area between 280 and 600 °C corrected by the fraction of H-form Te following equation (10) ($C \approx 0.1$ at 280 °C and ≈ 1 at 600 °C, as shown in figure 7) is 4.6 kJ mol⁻¹ and in good agreement with the transition enthalpy just obtained. As seen from equation (1), the ratio, $m\Delta H/\Delta H$, gives the number of atoms, m , which change their local structure co-operatively. m is 14.3 corresponding to the coordination number related to the second minimum in the radial distribution function. Thus it may be supposed that a local change occurs over a group of atoms involving the adjacent chain molecules in agreement with the microscopic model by Cutler and his co-workers.

Figure 7 shows the temperature dependence of the fraction of H-form Te, where the variation of the first coordination number is also plotted (Menelle *et al* 1987, 1989). In general the coordination number decreases in the supercooled region just below the melting point and becomes less than 2.5 above 400 °C, while the present results predict that such a steep decrease would occur around 350 °C. This discrepancy may appear very large; however, it should be pointed out that it is not easy to determine the coordination number to within 0.5, and the result is very much dependent on a method adopted. Recently, a molecular dynamics study (MD) on the structure of liquid Te has been reported (Hafner 1990), in which the structure of liquid Te at 450 °C is visualized as a network of entangled broken chains. The results indicate that the bond-angle distribution has a single well-defined peak at an angle of 100° while a peak in the dihedral angle distribution shown for liquid Se (Hohl and Jones 1990) has been completely

smear out. Since liquid Te at its melting point is almost in the H-form ($C \sim 0.87$ as shown in figure 7) the MD results may not contradict the present experiments. Then it would be of interest to see whether or not a non-random distribution of the dihedral angle develops upon lowering the temperature to the supercooled region where Te transforms to a structure isomorphous with Se.

In summary, we have for the first time confirmed the thermodynamic transition of liquid Te in the supercooled temperature region manifested by the extremum in the specific heat, the compressibility and the thermal expansion coefficient. It is shown that the Ehrenfest relations are satisfied among these thermodynamic functions. The results indicate that the structural change of liquid Te can be described by a single-order parameter to a first approximation. The inhomogeneous structure model explains the essential feature of the thermodynamic functions associated with the structural transition.

Acknowledgment

The author thanks Mr F Kakinuma for supplying him with the numerical data for the specific heat of Te measured with an adiabatic scanning calorimetry and for stimulating discussion. He would like to dedicate this paper to E F W Seymour who died suddenly on 22 December 1990.

References

- Bellissent R and Tourand G 1981 *Condensed Matter Physics* vol 2, ed J T Devreese, L F Demmers, V E Van Daren and J Van Royer (New York: Plenum) p 149
- Cabane C and Friedel J 1971 *J. Physique* **32** 331
- Cutler M, Kao S S and Silva L A 1990 *Phys. Rev.* **41** 3339
- Cutler M and Rasolondramanitra H 1985 *Localization and Metal-Insulator Transitions* ed H Fritzsche and D Adler (New York: Plenum) p 119
- Enderby J E and Gay M 1980 *J. Non-Cryst. Solids* **35/36** 1269
- Gaur U, Shu Hua-cheng, Mehta A and Wunderlich B 1981 *J. Phys. Chem. Ref. Data* **10** 89
- Hafner J 1990 *J. Phys.: Condens. Matter* **2** 1271
- Hohl D and Jones R O 1990 *J. Non-Cryst. Solids* **117/118** 922
- Iida T and Guthrie R L 1988 *The Physical Properties of Liquid Metals* (Oxford: Clarendon)
- Ioffe A F and Regel A R 1960 *Prog. Semicond.* **4** 238
- Kakinuma F and Ohno S 1987 *J. Phys. Soc. Japan* **56** 619
- 1988 *Z. Phys. Chem., NF* **156** 265
- Medzhidov R A and Rasulov S M 1975 *Izv. Akad. Nauk* **11** 646
- Mencle A, Bellissent R and Flank A M 1987 *Europhys. Lett.* **4** 705
- 1989 *Physica B* **156/157** 174
- Misawa M and Suzuki K 1980 *J. Physique Coll. Suppl.* **41** C8 203
- Perepezko J H and Paik J S 1984 *J. Non-Cryst. Solids* **61/62** 113
- Shimoji M 1977 *Liquid Metals* (London: Academic)
- Sullivan P J and Seidel G 1968 *Phys. Rev.* **173** 679
- Takeda S, Okazaki H and Tamaki S 1987 *J. Phys. Soc. Japan* **56** 1987
- Takimoto K and Endo H 1982 *Phys. Chem. Liq.* **12** 141
- Thurn H and Ruska J 1976 *J. Non-Cryst. Solids* **22** 331
- Tsuchiya Y 1986 *J. Phys. C: Solid State Phys.* **19** 1389
- 1988a *J. Phys. Soc. Japan* **57** 3851
- 1988b *J. Phys. C: Solid State Phys.* **21** 5473
- 1991 *J. Phys. Soc. Japan* **60** 960
- Tsuchiya Y and Seymour E F W 1982 *J. Phys. C: Solid State Phys.* **15** L689
- 1985 *J. Phys. C: Solid State Phys.* **18** 4721