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Thermodynamics of liquid-liquid crossover transition in liquid $Si_{15}Te_{85}$ eutectic alloy

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Abstract. Specific heat of liquid $Si_{15}Te_{85}$ was measured using both the adiabatic scanning calorimetry and modulation calorimetry. The specific heat has a very broad peak around 660°C of which the peak value is 46 J/mol.K. The results are totally different from the previous results that the specific heat is as large as 140 J/mol.K at the liquidus temperature and decreases rapidly with raising temperature. Combining the molar volume and sound velocity as a function of temperature, the thermodynamic susceptibilities, i.e. constant pressure specific heat, isothermal compressibility and thermal expansion coefficient, have been evaluated. Their temperature dependences and magnitudes are in good accordance with the predictions for a crossover transition in a liquid. Comparison is made to a liquid-liquid crossover transition in $Ge_{15}Te_{85}$ which is sharpest among crossover liquid-liquid transitions of this kind so far found.

1 Introduction

The eutectic Ge-Te alloy (~15 at.% Ge) undergoes the sharpest crossover transition so far found. The transition is manifested by a pronounced exremum in the three thermodynamic susceptibilities (constant pressure specific heat, C_p, isothermal compressibility, κ_T, and thermal expansion coefficient, α_p) [1]. One of the present authors (Y. T.) have shown that the peak values of these thermodynamic susceptibilities are interconnected by the thermodynamic relations known as the Ehrenfest-Pippard relations in the extended forms [2]. One of the relations is that the Prigogine-Defay ratio, $R = \delta C_p \delta\kappa_T/(\delta\alpha_p^2 TV)$, is unity, where δ refers to the quantity associated with the crossover transition. The constant pressure specific heat, C_p, isothermal compressibility, κ_T, and thermal expansion coefficient, α_p of liquid $Ge_{15}Te_{85}$ satisfy this relation. It implies that if structural changes cause a peak in C_p, a peak should appear also in κ_T and α_{ps}. Although the sign of a peak in κ_T is definitely positive by the thermodynamic requirements, a peak in α_p can be positive or negative. However, only structural changes with a negative peaked α_p have been found so far.

The Si-Te system in Te rich side forms an eutectic alloy at about 15 at.% Si and the eutectic temperature is 380°C, which compares 385°C for the eutectic Ge-Te alloy [3]. Since both Si and Ge belongs to the same IV group of the periodic table and both chemical properties are more or less similar, crossover transitions occurring in the liquid Ge-Te system would be expected also in the liquid Si-Te system. The thermodynamic measurements so far reported have indicated that the transitions actually take place [4]. The molar volume contracts over 200 K around 650°C and the resultant α_p has a very broad negative peak well above the eutectic temperature. The adiabatic compressibility estimated using the sound velocity and density shows a broad peak in the same temperature range in agreement with the thermodynamic relations. C_p measured by Schmid and Sommer is quite controversial, however [5]. It is as large as 140 J/mol.K at the eutectic temperature and monotonically decreases and no indication of a peak around 650°C has been reported.

In this paper we report C_p of $Si_{15}Te_{85}$ measured with the adiabatic scanning calorimetry and modulation calorimetry. The specific heat, C_p, has a very broad peak around 660°C and its peak value is as small as 46 J/mol.K in accord with other thermodynamic susceptibilities. Combining the molar volume and sound velocity as a function of temperature, the thermodynamic susceptibilities, i.e. constant pressure specific heat, isothermal compressibility and thermal expansion coefficient, have been evaluated. Their temperature dependences and magnitudes are in good accordance with the predictions for a crossover transition in a liquid [2]. Comparison is made to a liquid-liquid crossover transition in $Ge_{15}Te_{85}$ which is sharpest among crossover liquid-liquid transitions of this kind so far found [1].

2 Experimental procedure

Since the details of experimental procedure have been published elsewhere [1,6], only essential points are described in the following.

The $Si_{15}Te_{85}$ sample was made from both 6 nine grades Si and Te lumps. They were alloyed in an evacuated fused silica tube with 8mm inner diameter at about 1000°C and then quenched in water to form glassy alloy. The crushed glass was then sealed in a fused silica cell for measurements.

The heat capacity above the liquidus temperature was determined using an adiabatic scanning calorimeter. It consisted of ULVAC SH3000 calorimeter, Keithley 2182 nano-voltmeter and Ohkura EC 5700 digital temperature controller. The size of the fused silica cell was about 1.7 cm in diameter and 2.3 cm in height in which approximately 0.1 mol of alloy was sealed. In this calorimeter, a sample was continuously heated by supplying constant electric power under adiabatic condition and the resultant temperature increase was measured at every 30 s. The electric heat of 0.4 or 0.5 W was supplied and the heating rate was less than 0.8K/min, the condition of which was employed by finding that results were not dependent on these heating rates. The results of the heat capacity of liquid tin using this calorimeter are in agreement within to 3% of the compiled data without any calibration procedure.

The heat capacity below 600°C was also measured by a modulation calorimeter, ULVAC ACC-1. We used very small amount of sample, totally less than 2mg, consisting of a sample and a capillary fused silica cell of typically 0.05cm in diameter and 1cm in length. Therefore we could measure the heat capacity of a sample around the melting point with better temperature resolution than the adiabatic method. The frequency used was 1 Hz to ensure that the results were not affected by the thermal diffusivity of the specimen. The sample was suspended by a Chromel-Alumel thermo-couple with 25 μm in diameter with which the modulated temperature oscillations were detected. After subtracting the contribution from the empty capillary and the thermocouple, the net signal intensity in the solid state close to the melting point was scaled using the results obtained by the adiabatic method. The overall uncertain of the heat capacity in the liquid state, which was estimated with the reproducibility of the results obtained by different samples, was 5 %.

3 Results and Discussion

Fig. 1 shows the specific heat of $Si_{15}Te_{85}$ as a function of temperature. The results in the liquid state obtained with two different methods are in reasonably agreement. With the modulation calorimetry, the peak reflecting the endothermic reaction upon melting is much sharper and its intensity is smaller. These results come from the characteristics of modulation calorimetry [7]: the temperature resolution is better but it is insensitive to the latent heat caused by the first order phase transition. As plotted in the same figure, the data by Schmid and Sommer are totally different from the present results. The present results indicate that the specific heat at the vicinity to the melting point is 36 J/mol/K, increases gradually to make a broad maximum. The peak value is 44 J/mol/K at 655±3 °C.

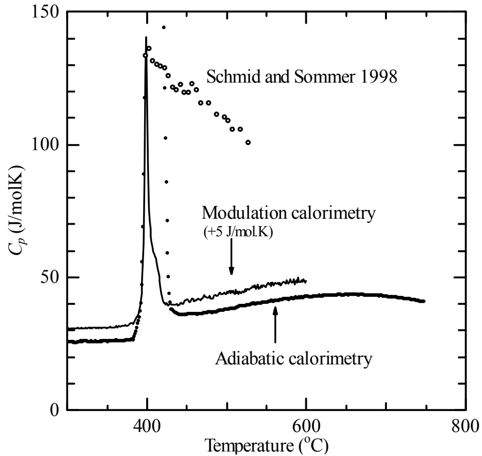

Fig. 1. Specific heat of $Si_{15}Te_{85}$. The results with the modulation calorimetry are shifted upwards by 5 J/mol.K.

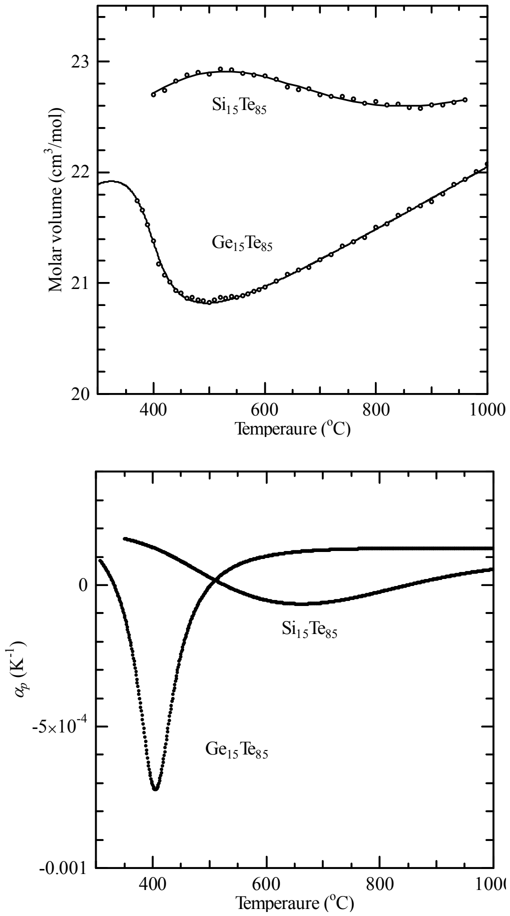

Fig. 2 Molar volume (upper figure) and thermal expansion coefficient (lower figure) for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$.

Figs. 2-4 compare the molar volume, V, constant pressure specific heat, C_p, adiabatic and isothermal compressibility, κ_S and κ_T, and thermal expansion coefficient, α_p, for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$. The molar volume contracts with increasing temperature over 300K interval for $Si_{15}Te_{85}$ and over 100K interval for $Ge_{15}Te_{85}$. The amount of volume contraction for $Ge_{15}Te_{85}$ is about 2 times as large as that of $Si_{15}Te_{85}$. It may be observed that all those thermodynamic functions for each alloy have the

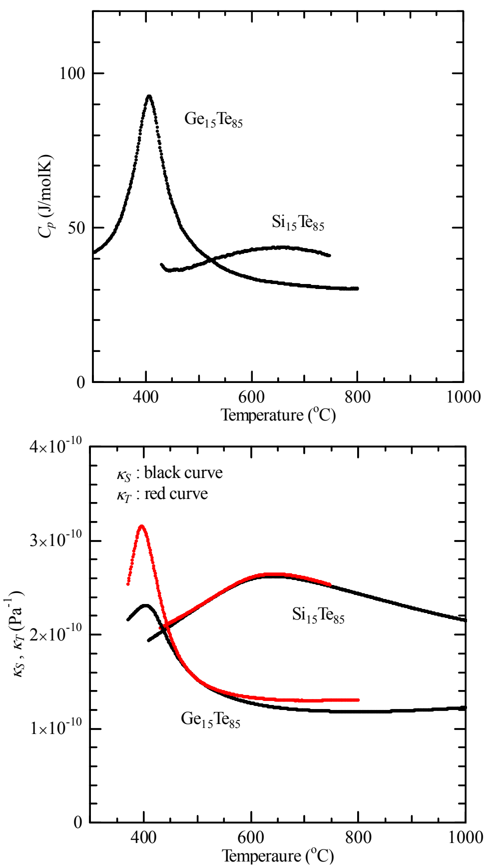

Fig. 3 Constant pressure specific, Cp, (upper figure) and compressibility for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$. Black curves denote the adiabatic compressibility, κ_S, and red curves the isothermal compressibility, κ_T.

common temperature characteristics; the extrema of C_p, κ_T, and α_p occur around the same temperature (referred to as T^*). T^* is 655±3 °C and 407±3 °C respectively for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$.

A close correlation among temperature dependences of the extrema of C_p, κ_T, and α_p is considered first. Since the detailed derivations have been published elsewhere [2], we look at the Prigogine-Defay ratio, defined by,

$$R_{PD} = \frac{\delta C_p \delta k_T}{TV\delta \alpha_p{}^2} \cdot \tag{1}$$

Here the δ symbol refers to a quantity caused by the structural changes or the magnitude of a positive or negative peak in the temperature variation of C_p, κ_T, and α_p. The Prigogine-Defay ratio, R_{PD}, becomes unity when the structural changes dominate the temperature dependences of these thermodynamic functions. However, it is not easy to partition the peak from the base line, which is expected if there were no structural change, without using a particular model. In stead of doing so, we use α_p-C_p and α_p-κ_T plots of which the respective slopes give rough estimates of the ratio $\delta C_p/\delta\alpha_p$, and $\delta\kappa_T/\delta\alpha_p$. Figs. 4 shows, respectively, the results for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$. The duplex plots are

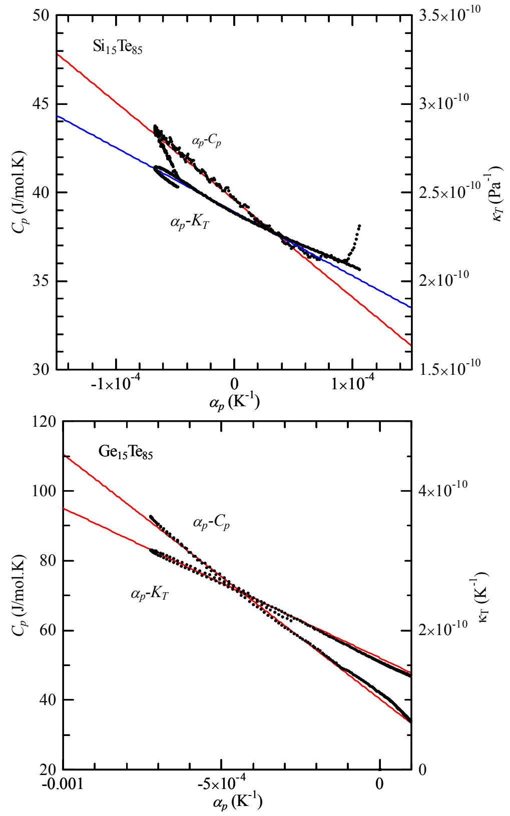

Fig. 4. α_p-C_p, and α_p-κ_T plots for $Si_{15}Te_{85}$ (upper figure) and $Ge_{15}Te_{85}$ (lower figure). The respective slopes of these plots give the value of $\delta C_p/\delta\alpha_p$ and $\delta\kappa_T/\delta\alpha_p$.

resultant of either temperature difference of two independent measurements and/or temperature variations of base lines for respective thermodynamic quantities. The slope of α_p-C_p plot is (5.51±0.18)×10^4 Jmol^{-1} for $Si_{15}Te_{85}$ and (7.02±0.02)×10^4 Jmol^{-1} for $Ge_{15}Te_{85}$. The slope of α_p-κ_T plot is (3.26±0.029)×10^{-7} Pa^{-1}K for $Si_{15}Te_{85}$ and (2.15±0.016)×10^{-7} Pa^{-1}K for $Ge_{15}Te_{85}$. Putting these values into equation (1) together with the molar volume and temperature at extrema, R_{PD} is 0.94±0.042 and 1.04±0.008 respectively for $Si_{15}Te_{85}$ and $Ge_{15}Te_{85}$. Keeping in view the crudeness of the assignments to the base line, it may be concluded that the Prigogine-Defay ratio is unity and therefore the observed close correlation among the temperature dependences of C_p, κ_T, and α_p is a consequence of the structural changes in the melt.

Rapid structural changes in a binary mixture inevitably induce concentration fluctuations. The concentration fluctuations at zero wave length limit, $S_{cc}(0)$, is the reciprocal of the Darken stability, D, as RT/D (R: the universal gas constant). In the temperature-concentration domain of structural transitions, the excess part, δD is induced by structural changes [2]. δD is connected to δC_p as

$$\delta D = -T^{-1}(\partial T/\partial x)_{p,C}{}^2\,\delta C_p \ , \tag{2}$$

where C is the extent of the structural change. It should be noted that δD is definitely negative. This relation predicts that the stability of a binary mixture decreases in the concentration-temperature domain of structural change and concentration fluctuations develops where δC_p has a large peak, unless $(\partial T/\partial x)_{\mathrm{p,C}}$ vanishes. As reported previously, $(\partial T/\partial x)_{\mathrm{p,C}}$ is very small around $Ge_{15}Te_{85}$ whereas it is very large for $Si_{15}Te_{85}$ [1,5]. This implies that the structural change in the latter melt induces large concentration fluctuations and thus can explain why the peak breadth of C_p for $Si_{15}Te_{85}$ is very large as compared with that for $Ge_{15}Te_{85}$.

4 Conclusion

Specific heat of $Si_{15}Te_{85}$ was measured with adiabatic and modulation carolimetry. Both results are in reasonably agreement. The specific heat just above the melting point is 36 J/mol/K, increases gradually to make a broad maximum. The peak value is 44 J/mol/K at 655±3 °C. The present results are consistent with the temperature dependences of the thermal expansion coefficient, sound velocity and compressibility. The Prigogine-Defay ratio is unity within experimental uncertainty. It is concluded that liquid-liquid crossover transition can consistently explain the correlation among the thermodynamic functions.

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