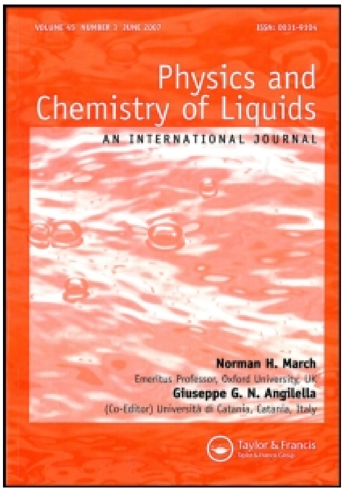

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Robert Castanet[a]; Claire Bergman[a]
[a] Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S., Marseille, France

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Experimental Evidence From Heat Capacity Measurements of a Transition in the Vicinity of the Melting Temperature in a Liquid Eutectic GeTe Alloy

ROBERT CASTANET and CLAIRE BERGMAN

Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S., 26, rue du 141ème R.I.A., 13003 Marseille, France.

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The temperature dependence of the enthalpy of the Te-rich eutectic Ge–Te alloy was measured by drop calorimetry in the crystalline, amorphous and liquid states using a high temperature Calvet calorimeter. This dependence leads to a second order transition which takes place around the eutectic temperature. Such a behaviour is explained by the destruction of the short range order in the liquid phase by heating.

1 INTRODUCTION

The germanium–tellurium system has a particularly large ability to give glasses when tellurium-rich compositions are quenched from the melt. This capacity, maximum for the eutectic composition[1] since massive glasses can be obtained by water quenching, seems to be connected with chemical ordering in the liquid state.

As heat capacities are very sensitive to structural modifications,[2] a calorimetric study of these alloys was undertaken on both sides of the melting point. The temperature dependence of the enthalpy of the $Ge_{0.15}Te_{0.85}$ alloy (eutectic composition) was measured by drop calorimetry from 600 to 1100 K and then the heat capacities were deduced by derivation. A similar work was carried out on $Ge_{0.5}Te_{0.5}$ alloys.[5]

On the other hand, calorimetric measurements were performed on glassy $Ge_{0.16}Te_{0.84}$ alloys by drop calorimetry and differential scanning calorimetry.[6] The crossing of the vitreous transition enables us to obtain supercooled liquids in an unusual range. The aim of this work was to compare the thermodynamic behaviour of the Ge–Te alloys in different structural states at two compositions, one corresponding to the compound $x_{Te} = 0.5$, and the second to the eutectic composition† $x_{Te} = 0.85$.

2 EXPERIMENTAL

2.1 Sample preparation

The pure metals (metallic impurities less than 10^{-3} mass %) used for the preparation of the $Ge_{0.15}Te_{0.85}$ sample were purchased from Koch–Light. The components, placed after weighing in a glassy silica tube, were then reacted together by melting. After homogenization by successive melting and solidification cycles, the solid alloy was annealed for a week at 600 K and then slowly cooled to room temperature. The whole preparation process was made under pure argon atmosphere.

2.2 Calorimetric measurements

The measurements were carried out with a high-temperature Calvet calorimeter. The determination of the enthalpy difference $\Delta_{298}^{T}h = h(T) - h(298)$ was performed by dropping solid samples (~ 100 mg) at 298 K into the calorimetric cell at T under pure argon atmosphere.[5] The experimental procedure, similar to that used for the direct reaction calorimetry, was described previously.[7] For each value of T, the measurements were repeated about ten times. The calorimeter was calibrated by adding small quantities of National Bureau of Standards–alumina[8] into the melt after each series of measurements.

3 RESULTS

The direct results (mean value at each temperature from ten experiments) are given in Table I and shown on Figure 1. The enthalpy jump between 638 and 648 K corresponds to the eutectic temperature, $T_m = 648$ K, according to (4). We did not observe the enthalpy variation due to the reaction

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† According to the literature, the eutectic composition lies either at $x_{Te} = 0.84$[3] or 0.85.[4] In this work, it is assumed that this deviation is negligible.

TABLE I

Enthalpy variation between 298 K and T of liquid or solid eutectic alloy $Ge_{0.15}Te_{0.85}$ (primary results)

T/K	$\Delta_{298}^{T}h$/kJ mol^{-1}	T/K	$\Delta_{298}^{T}h$/kJ mol^{-1}
614	7.90	769	29.04
638	8.77	818	30.47
648	17.66	863	32.39
655	18.85	923	34.49
667	21.87	974	36.41
678	22.52	1025	38.51
717	26.46	1079	40.11

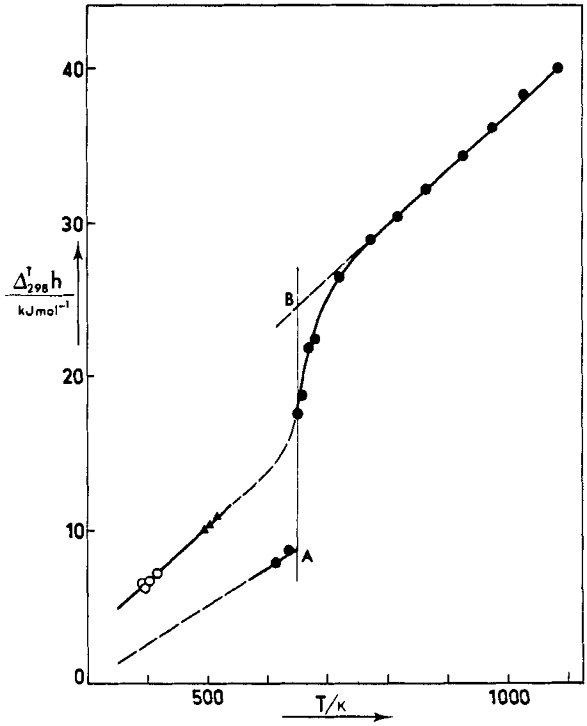

Figure 1 Molar enthalpy variation, $\Delta_{298}^{T}h$, from 298 to T of the Te-rich eutectic of Ge–Te alloys in the crystalline, supercooled and stable liquid states with respect to T. ● stable states (drop method), ○ supercooled liquid (drop method), ▲ supercooled liquid (differential scanning calorimetry).

$GeTe(\gamma) \rightarrow GeTe(\alpha)$ which takes place at 638 K according to (4). Below T_m, the derivation of $\Delta_{298}^{T} h$ with respect to temperature yields the heat capacity value of the solid phase, $C_p = 32.8$ J K^{-1} mol^{-1}. This value compares well with that calculated from the heat capacities of α-GeTe (33.8 J K^{-1} mol^{-1}),[5] and of pure Te (33.5 J K^{-1} mol^{-1}),[9] which are the corresponding phases in equilibrium[4] which amounts 33.6 J K^{-1} mol^{-1}. However, both values are very different from that of de Neufville[10] (24.7 J K^{-1} mol^{-1}).

Concerning the eutectic phase, its enthalpy and entropy of melting, h^m and s^m, can be calculated from the jump of the heat content at 648 K:

$$h^m = \Delta_{298}^{648} h(l) - \Delta_{298}^{648} h(s) = 8.64 \text{ kJ mol}^{-1}$$

and

$$s^m = 13.33 \text{ J K}^{-1} \text{ mol}^{-1}.$$

The value of the enthalpy of melting of de Neufville[10] (9.2 kJ mol^{-1}) agrees reasonably well with ours.

The heat capacity of the liquid phase can be deduced in the same way. We can see on Figure 1 that $C_p(l) = \delta/\delta T(\Delta_{298}^{T} h)$ depends strongly on T just above the melting point i.e. in the 648–780 K temperature range. For $T > 780$ K, $\Delta_{298}^{T} h(l)$ varies linearly with respect to T and $C_p(l)$ becomes temperature-independent.

The C_p-values obtained by numerical derivation are given in the second column of Table II. The corresponding excess heat capacity values, C_p^E (departure from the Kopp–Neumann rule):

$$C_p^E = C_p - 0.15 C_p(\text{Ge}, l) - 0.85 C_p(\text{Te}, l)$$

were calculated using temperature independent values for liquid Ge (27.6 J K^{-1} mol^{-1}) and liquid Te (37.7 J K^{-1} mol^{-1}) taken from Hultgren *et al.*[9] They are also given in Table II (column 3).

TABLE II

Heat capacity, C_p, and excess heat capacity, C_p^E, of the liquid eutectic alloy $Ge_{0.15}Te_{0.85}$

T/K	C_p/J mol^{-1} K^{-1}	C_p^E/J mol^{-1} K^{-1}
650	219	183
670	155	119
690	96	60
710	64	28
730	47	11
750	41	5
770	37	1
790	36	0

4 DISCUSSION

Our measurements of the heat contents in the liquid phase lead to heat capacity values which fall sharply from unusually high values just above the eutectic temperature up to 780 K. If we consider the experimental points obtained from the supercooled range it can be seen (Figure 1) that the whole curve can be divided into two parts: a high and a low temperature parts where C_p is constant and equal to 36 J K^{-1} mol^{-1} (this work), and 35 J K^{-1} mol^{-1};[6] the first part corresponds to the stable liquid and the second one to the supercooled liquid.

Between these two regions, there is a second order transition which occurs around the eutectic temperature but it could be accidentally if we admit that the liquid phase has its peculiar behaviour which doesn't take into account that of the solid one.

Then the very strong variation experimentally observed on the liquid heat capacities is probably a part of the whole transition phenomenon unobserved under usual experimental conditions. This transition takes place on a temperature range of about 150 K above the eutectic point; although slightly shifted towards lower temperature, it was indicated by de Neufville too.[10] Yet, our maximum C_p-value (220 J K^{-1} mol^{-1}) is larger than the maximum given by de Neufville. These discrepancies can be explained partially by the difference in composition and mostly by kinetic factors in DSC measurements.

Another point can be accounted for in terms of the existence of associations in the liquid phase. It is possible to calculate a value of the enthalpy of melting of the eutectic phase, $Ge_{0.15}Te_{0.85}$ by adding the corresponding values of the solid phases in equilibrium just below T_m i.e. 0.3 α-$Ge_{0.5}Te_{0.5}$ and 0.7 Te; the enthalpy of melting of α-$Ge_{0.5}Te_{0.5}$ at 648 K is obtained by extrapolation of our enthalpic measurements of the liquid phase at lower temperature. The calculation yields:

$$h^m(\alpha\text{-}Ge_{0.5}Te_{0.5}, 648\ K) = 11.43\ kJ\ mol^{-1}$$

and using for h^m(Te) the Hultgren's data,[9] we obtained:

$$h^m_{Add}(Ge_{0.15}Te_{0.85}) = 15.67\ kJ\ mol^{-1}$$

This value is much larger than the value we obtained experimentally in this work, i.e.:

$$h^m(Ge_{0.15}Te_{0.85}, 648\ K) = 8.64\ kJ\ mol^{-1}$$

This can be interpreted as an incomplete destruction of bounds while the melting occurs, leaving some short range order in the corresponding liquid.

Moreover, if we consider the enthalpy difference no longer with the actual data but with extrapolated data from high temperature liquid phase at 648 K i.e. $h_B - h_A$ on Figure 1, we find 15.50 kJ mol^{-1} which is very close to the additive value calculated above. At high temperature, the liquid is totally disordered and obeys the additivity rule.

5 CONCLUSION

The heat capacity of the $Ge_{0.15}Te_{0.85}$ liquid alloy is shown as a function of T on Figure 2 as well as that of the $Ge_{0.5}Te_{0.5}$ melt.

From about 780 K upwards, C_p of the eutectic alloy obeys the Kopp–Neumann rule whereas it is not the case for the equiatomic composition. This is in agreement with the end of the short range order–disorder reaction in the eutectic liquid. Since for $T > 780$ K the heat capacity of the melt can be calculated assuming only pure Te and Ge species ($C_p = 36.2$ J K^{-1} mol^{-1}), the behaviour of the liquid phase can be interpreted as a chemical equilibrium between associated entities and pure species. In the framework of

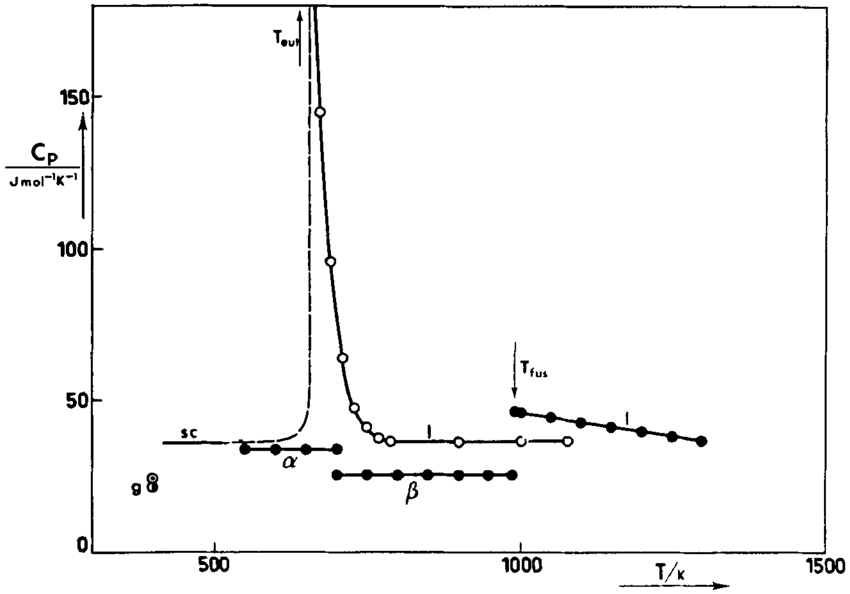

Figure 2 Molar heat capacity, C_p, of the Te-rich eutectic (○, ⊙) and $Ge_{0.5}Te_{0.5}$ compound (●) in the crystalline, glassy, supercooled and liquid states with respect to T. ● $Ge_{0.5}Te_{0.5}$ (α, β and liquid), ○ Te-rich eutectic, ◑ glassy alloy,[6] ⊙ glassy alloy.[10]

an associated model previously developed,[11] we could interpret the enthalpy variation as due to the decrease of the number of associates, N_c, with increasing temperature. The excess heat capacity of the melt can be written as follows:

$$C_p^E = C_p - \sum x_i Cp_i = \Delta H_0 \frac{\partial N_c}{\partial T}$$

An S-shaped curve, as experimentally obtained here, was calculated from the model. Concerning the stoechiometry of the associations, it could be "$GeTe_2$" as proposed by de Neufville who introduced in the Ge–Te system the concept of binary and ternary sites according to the bonding model of Cabane and Friedel for liquid tellurium.[12]

In the same temperature range, a transition was observed by de Neufville in resistivity measurements interpreted as a change from semiconducting to metallic behaviour.

From Figure 2, we can see that the behaviour on melting of both compositions is quite different indicating different involved mechanisms.

Indeed, the α-$Ge_{0.5}Te_{0.5}$ crystalline phase (rhomboedral structure) undergoes a first order transition to give another crystalline phase β-$Ge_{0.5}Te_{0.5}$ with a higher symmetry (fcc-NaCl structure) and then melts at 997 K. According to the observed variation of C_p of the liquid phase, the liquid behaves according to the additivity rule.

In the case of the eutectic composition to which no unique solid phase corresponds, the eutectic temperature coincides with the disordering reaction observed in the supercooled and liquid phase as indicated above.

It could be asked the question of the influence of the composition on this phenomenon; it is often admitted that the eutectic range, in particular the tellurium-rich ones, could have a peculiar short range order.[13]

Concerning the glassy samples, the heat capacity values obtained in the previous work[6] for g-$Ge_{0.16}Te_{0.84}$ (21.5 J mol^{-1} K^{-1}) is in agreement with de Neufville's value; in his paper, he pointed out that this value is very similar to that of crystalline sample which results from the crystallization. Yet, this value compares well with that of c-$Ge_{0.5}Te_{0.5}(\beta)$ which is 24.5 J mol^{-1} K^{-1} but is different from that given in this work for c-$Ge_{0.15}Te_{0.85}$ (32.8 J mol^{-1} K^{-1}) which is nearly the same as the value of c-$Ge_{0.5}Te_{0.5}(\alpha)$. This comparison indicates that the glassy eutectic samples crystallize towards the high temperature β phase and not the α low temperature which is however a part of the crystalline eutectic. Then, when cooling the liquid phase, depending on which crystalline form is present in competition, glassy or crystalline material will be obtained.

These conclusions can be brought together those drawn from neutron diffraction measurements of Uemura *et al.*[14] These authors conclude that the structure of amorphous $Ge_{0.5}Te_{0.5}$ differs considerably from the liquid state, which is not the case of As_2Te_3, studied in the same work.

Further diffusion measurements on the structure of glassy Ge–Te sample of both compositions could be of interest to clear up these conclusions.

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