Heat Contents of Four Au-Te Alloys

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ABSTRACT

The heat content of four Au-Te alloys in the solid and liquid states from 298K to T (~400<T/K<~900) were measured on heating (drop method) with the help of a high temperature Tian-Calvet calorimeter. The heat capacities of both liquid and solid alloys as well as their enthalpies of melting were deduced.

We pointed out in a previous paper that the enthalpy of mixing of the Au-Te melts undergoes a transition in a very narrow temperature range. Such a transition cannot be explained by the destruction of some chemical order since the enthalpy of formation is only very weakly negative (~ -1 $kJ.mol^{-1}$ at the minimum). Then we calculated from our experimental data $\delta\Delta H = \Delta H^m - \Sigma x_i \Delta H_i^m$, which is the difference between the experimental enthalpy of melting, ΔH^m, and the enthalpy of melting calculated according to the additivity, $\Sigma x_i \Delta H_i^m$. Indeed, $\delta\Delta H$ is a thermodynamic function very sensible to residual short-range order after melting. We showed previously that $\delta\Delta H$ is strongly negative (-6.5 and -7.1 $kJ.mol^{-1}$) for the associated systems Ag-Te and Cu-Te respectively. In the case of the Au-Te alloys, $\delta\Delta H$ is positive for the five compositions which means that there is no residual short-range order after melting.

KEY WORDS

Calorimetry, Enthalpy, Heat Capacity, Au-Te

1. INTRODUCTION

In a previous paper /1/, we investigated the thermal behaviour of two eutectic alloys (Cu-Te and Ag-Te) belonging to strongly associated alloys in the liquid state as shown by their highly negative enthalpy of mixing. The phase diagrams of these two systems show only one congruently high-temperature melting compound (Ag_2Te and Cu_2Te) whose stoichiometry corresponds to the normal valencies of the pure components. Moreover, the strong minima of the enthalpy of formation of the liquid phase, located at this stoichiometry, suggest the existence of associations in the liquid state corresponding to these compounds. The enthalpy does not depend on temperature in the investigated temperature range.

On the contrary, there is another class of alloys (for example Ge-Te, Au-Pb, Au-Te, Au-Sb), exhibiting intermediate compounds but with low-temperature melting point. These melts often exhibit what we called a "*short-range order-disorder transition*" /2/, i.e., a strong increase of their enthalpy of formation in a narrow temperature range (positive excess heat capacity). In the case of the Ge-Te melts, Castanet *et al.* pointed out /3/ the occurrence of such a transition at the Te-rich eutectic composition. However, in many cases such a transition cannot be completely explained by the existence of associations corresponding to the congruently melting compound. In particular, their low melting eutectics often show a complex behaviour as for the Ge-Te system. The aim of our work, therefore, is to investigate the thermodynamic behaviour of this

class of melts. As a first step we report here the results obtained on the Au-Te alloys.

In two previous papers, we reported the results of our measurements of the enthalpy of formation of the Au-Te liquid alloys /4/ by direct reaction calorimetry and of the free enthalpy of formation /5/ by Knudsen effusion combined with a mass-spectrometer. The phase diagram calculated from the thermodynamic functions of the liquid and solid phases agrees well with the experimental one. The enthalpy of mixing changes its sign with composition and becomes positive on the Au-rich side and less negative with increasing temperature on the Te-rich side. In the composition range investigated ($0.5 \leq x_{Te} \leq 1$), the enthalpy of formation does not depend on temperature neither from 737 to 819 nor from 872 to 1000K. However, it increases between 819K (h^f_{min} = -1.01 kJ.mol^{-1} at x_{Te} = 0.63) and 872K (h^f_{min} = -0.63 kJ.mol^{-1} at x_{Te} = 0.69). We also determined the heat content of the $AuTe_2$ compound in the solid and liquid state /6/ by the same method used here. The heat capacity of the melt is temperature independent between the melting point of the compound and 923K and above 923K again but undergoes a sudden decrease at this temperature.

2. APPARATUS AND METHOD

The coordinates of the two investigated Au-Te eutectic alloys are x_{Te} = 0.53, T = 720K and x_{Te} = 0.88, T = 689K respectively according to /7/. We also studied two alloys (x_{Te} = 0.60 and 0.77) on both sides of the compound. The solid alloys were synthesised by melting together the pure components in suitable proportions. The pure metals used were purchased from Koch-Light with metallic impurities less than 10^{-3} mass%. They were placed in a quartz ampoule sealed under vacuum. After some cycles of fusion-crystallization, they were annealed in the solid state for two days about 10K below their melting temperature and then slowly cooled down at room temperature. Their melting points were verified by differential calorimetric analysis.

The apparatus employed for the measurements was a high-temperature (T/K < 1400) Tian-Calvet calorimeter. The drop method used has already been described /8/. The molar heat content variations of the samples from 298K to T were deduced from the heat effects corresponding to drops of solid samples (~50 mg) at a temperature near 298K into an empty graphite crucible placed in the laboratory cell of the calorimeter at temperature T under argon atmosphere. The measurements were repeated about ten times for each temperature. The calibration of the calorimeter was performed by adding some small pieces of α-alumina (U.S. National Bureau of Standards, U.S.A.), the enthalpy change of which from T_0 to T is well-known /9/.

3. RESULTS

3.1. The Au-rich eutectic (x_{Te} = 0.53).

The values of the enthalpy of the Au-rich eutectic from 487 to 894K are given in Table 1 and shown in Figure 1. In the solid state (T ≤ 722K) our experimental data were linearly fitted according to the following equation:

$$H(T)-H(298K) / kJ.mol^{-1} = -8.41 + 0.0277\ T$$

Then $$Cp(s) / J.K^{-1}.mol^{-1} = 27.7 \pm 0.8$$

The results obtained in the liquid state can be represented according to the following equation:

Table 1

Heat content of the Au-rich Au-Te eutectic (x_{Te} = 0.53, T_0 = 298K) with respect to temperature

T (K)	H(T)-H(298K) (kJ.mol-1)	T (K)	H(T)-H(298K) (kJ.mol-1)
487	4.9	764	30.8
514	5.6	778	31.7
534	6.2	793	31.4
573	7.3	806	31.7
625	8.7	820	32.6
717	12.1	834	32.7
722	29.3	855	33.9
732	30.1	871	34.4
741	30.6	883	34.6
752	30.3	894	34.8

$H(T)-H(298K) / kJ.mol^{-1} = 26.42 - 0.0175\ T + 0.03\ 10^{-3}\ T^2$

$C_P(l) / J.K^{-1}.mol^{-1} = (-17.5 + 0.06\ T) \pm 0.9$

The jump at 722K which agrees well with the melting temperature derived from the literature leads to the following values of the enthalpy and entropy of fusion respectively:

$\Delta H^m = H(l, 722K) - H(s, 722K) / kJ\ mol^{-1} = 17.2 \pm 0.5$

$\Delta S^m / J.K^{-1}\ mol^{-1} = 23.8 \pm 0.8$

The eutectic melting process corresponds to the reaction:

$$n_{Au}Au(s) + n_C Au_{0.333}Te_{0.667}(s) \text{ -----> } Eut.(l)$$

where $C \equiv Au_{0.333}Te_{0.667}$. The molar quantities of Au and C are given by the lever rule. The enthalpy of melting, ΔH^m, can then be calculated as:

$$\Delta H^m = 0.205\ \Delta H^m(Au) + 0.795\ \Delta H^m(C) + h^f(eut., l) - 0.795\ h^f(C, l)$$

where h^f (eut., 1) and h^f(C, 1) are the enthalpies of formation of the eutectic and of the compound determined in a previous work /4/ as -0.342 and -1.082 $kJ.mol^{-1}$ respectively with reference to both liquid components. The enthalpy of melting of C was taken as 18.6 $kJ.mol^{-1}$ from this work and that of pure gold was taken from Hultgren *et al.* /10/ as 12.55 $kJ.mol^{-1}$. Then the calculated enthalpy of melting of the eutectic was found as 17.3 $kJ.mol^{-1}$ which is in good agreement with the experimental one (Figure 1, open square).

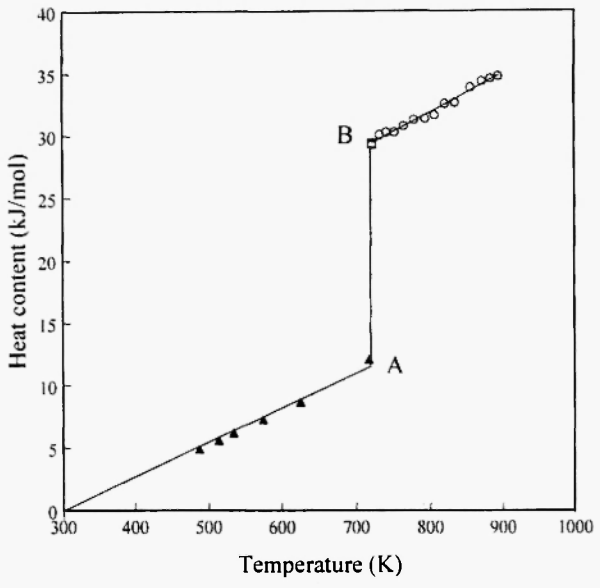

Fig. 1: Heat content of the Au-rich Au-Te eutectic (x_{Te} = 0.53, T_0 = 298K) with respect to temperature. Full triangles: solid state; Open circles: liquid state; Open square: calculated from the enthalpy of fusion and the heat content of the solid at 722K.

3.2. The Te-rich eutectic (x_{Te} = 0.88)

The heat content was measured in the 417<T/K<974 temperature range. The results obtained for the Te-rich eutectic (Table 2 and Figure 2) are similar to those of the previous one. In the solid state:

$$H(T)-H(298K) / kJ.mol^{-1} = -8.52 + 0.02756\ T$$

Then $C_P(s) / J.K^{-1}.mol^{-1} = 27.6 \pm 0.8$

The results obtained in the liquid state (687-974K) can be represented according to the following equation:

$H(T)-H(298K) / kJ.mol^{-1} = -2.256 + 0.05178\ T - 0.011\ 10^{-3}\ T^2$

and $Cp(l) / J.K^{-1}.mol^{-1} = (51.8 - 0.022T) \pm 1.0$

Table 2

Heat content of the Te-rich Au-Te eutectic (x_{Te} = 0.88, T_0 = 298K) with respect to temperature

T (K)	H(T)-H(298K) (kJ.mol-1)	T (K)	H(T)-H(298K) (kJ.mol-1)
417	3.1	740	31.0
468	4.4	757	31.1
518	5.7	772	31.0
586	7.5	797	32.1
673	10.1	807	33.2
681	10.3	823	32.0
687	27.7	837	33.3
691	27.7	854	33.1
698	28.4	869	35.0
705	28.7	898	35.7
713	29.8	933	36.5
722	30.2	961	37.6
728	29.7	974	38.1

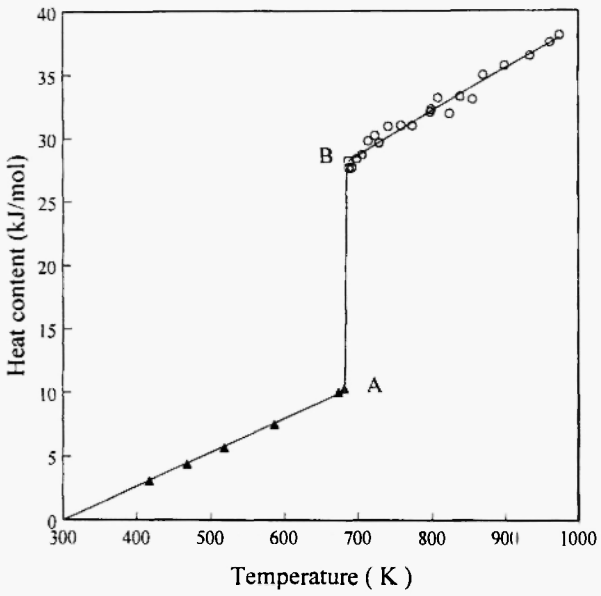

Fig. 2: Heat content of the Te-rich Au-Te eutectic (x_{Te} = 0.88, T_0 = 298K) with respect to temperature. Full triangles: solid state; Open circle: liquid state; Open square: calculated from the enthalpy of fusion and the heat content of the solid at 687K.

The jump at 687K agrees well with the melting temperature taken from the literature. It leads to the following values of the enthalpy and entropy of fusion respectively:

ΔH^m / kJ mol^{-1} = H(l, 687K) - H(s, 687K) = 17.38 ± 0.5

ΔS^m / J.K^{-1} mol^{-1} = 25.3 ± 0.8

As for the Au-rich eutectic, we calculated the enthalpy of melting of the alloy taking the data from the same references. We obtained in this way ΔH^m – 17.9 kJ.mol^{-1} which is very close to our experimental result (Figure 2, open square).

3.3. The x_{Te} = 0.60 alloy

The heat content was measured in the 677 < T/K < 898 temperature range (Table 3 and Figure 3). In the solid state (T < 718K):

H(T)-H(298K) / kJ.mol^{-1} = -7.97 + 0.0267 T

Then Cp(s) / J.K^{-1}.mol^{-1} = 26.7± 0.8

Table 3

Heat content of the x_{Te} = 0.60 Au-Te alloy (T_0 = 298K) with respect to temperature

T (K)	H(T)-H(298K) (kJ.mol-1)	T (K)	H(T)-H(298K) (kJ.mol-1)
677	9.9	764	30.8
694	10.6	768	30.5
707	11.0	773	31.2
717	11.3	797	31.5
718	20.4	804	32.3
720	21.1	816	33.0
724	27.8	829	33.3
734	28.9	857	34.4
744	30.2	879	36.5
754	30.7	898	37.9

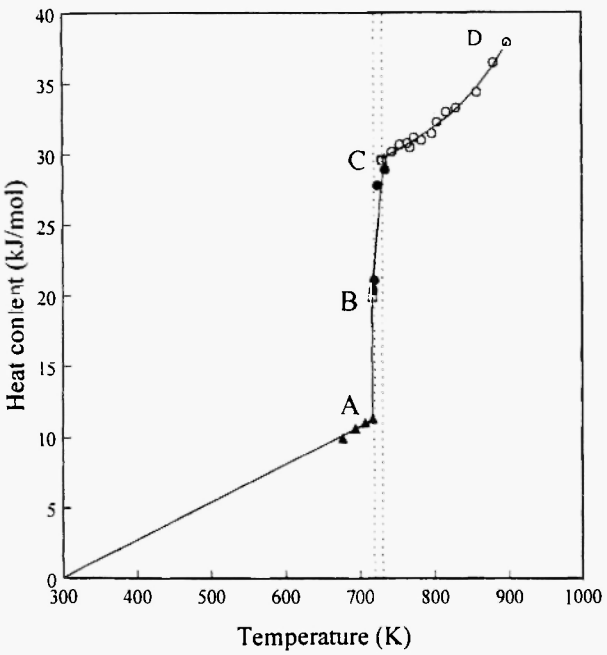

Fig. 3: Heat content of the x_{Te} = 0.60 Au-Te alloy (T_0 = 298K) with respect to temperature. Full triangles: solid state; Open circles: liquid state; Full circles: two-phase domain; Open squares: calculated from the eutectic reaction and the heat content of the solid at 718K (point B) and from the enthalpy of dissolution of the solid in the eutectic and the point B (point C).

The total enthalpy change between 717 (eutectic temperature) and 724K (liquidus temperature according to the phase diagram) is 17.6 kJ.mol^{-1}. Since the alloy does not melt congruently, this enthalpy includes two parts: the first one (isothermal), ΔH^{eut}, is due to the eutectic reaction at 718K, the second one (above 718K according to the phase diagram), $\Delta H(718K)-\Delta H(724K)$, corresponds to the further dissolution of the solid compound in the eutectic liquid. Then, taking into account our experimental results only, it was not possible at this stage to separate the two contributions. Thus, we performed the same calculations as for the eutectic alloys. The reaction occurring at the eutectic level can be written:

$$0.10\ Au(s) + 0.90\ Au_{0.333}Te_{0.667}(s) \text{ -----> } 0.49\ Eut(l) + 0.51\ Au_{0.333}Te_{0.667}(s)$$

i.e. $$0.10\ Au(s) + 0.39\ Au_{0.333}Te_{0.667}(s) \text{ -----> } 0.49\ Eut(l)$$

and ΔH^{eut} / kJ.mol^{-1} = 8.62 was calculated using the same references as for the previous alloys.

The enthalpic part which corresponds to the dissolution of the solid phase can be calculated too, neglecting any differences between the heat contents of the phases during the increase of temperature. It corresponds to the reaction:

$$0.49\ Eut(l) + 0.51\ Au_{0.333}Te_{0.667}(s) \text{ -----> } L(x_{Te}=0.6)$$

We found in such a way: $\Delta H(718K)-\Delta H(724K)$/kJ.mol^{-1} = 9.66. Adding this result to the enthalpy of eutectic reaction we obtained the overall enthalpy of melting as 18.28 kJ.mol^{-1} not so far from the experimental one (see Fig. 3). Then, the two-phase domain can be determined as shown in Fig. 3 (vertical dotted lines) and we could determine the enthalpy of the melt as:

$$H(T)-H(298K) / kJ.mol^{-1} = 111.38 - 0.2408\ T + 0.177\ 10^{-3}\ T^2$$

and $$C_P(l) / J.K^{-1}.mol^{-1} = (-240.8 + 0.354\ T) \pm 1.3$$

3.4. The $x_{Te} = 0.77$ alloy

The heat content was measured in the 390 < T/K < 880 temperature range (Table 4 and Figure 4). In the solid state (T < 672K):

$$H(T)-H(298K) / kJ.mol^{-1} = -8.08 + 0.0265\ T$$

Then $$C_P(s) / J.K^{-1}.mol^{-1} = 26.5 \pm 0.8$$

The overall enthalpy of melting of the alloy is 19.38 kJ.mol^{-1}. It is clear here that the results above the liquidus correspond to the open circles of Fig. 4 and the full squares of the figure to the two-phase alloy. The same calculations as for x_{Te} = 0.60 (open squares of Fig. 4), i.e., for the following reactions:

$$0.31\ Te(s) + 0.17\ Au_{0.333}Te_{0.667}(s) \text{ -----> } Eut(l)$$

$$0.48\ Eut(l) + 0.52\ Au_{0.333}Te_{0.667}(s) \text{ -----> } L(x_{Te}=0.77)$$

lead to:

$$\Delta H^{eut} / kJ.mol^{-1} = 8.77 \pm 0.3$$

and $$\Delta H(692K)-\Delta H(711K) / kJ.mol^{-1} = 9.87 \pm 0.3$$

Adding these two values yields 18.64 kJ.mol^{-1} for the overall enthalpy of melting which is close to the experimental one (19.38 kJ.mol^{-1}). Then, the enthalpy of the liquid can be fitted according to the following equation:

$$H(T)-H(298K) / kJ.mol^{-1} = -12.74 + 0.0734\ T - 0.021\ 10^{-3}\ T^2$$

and $$C_P(l) / J.K^{-1}.mol^{-1} = (73.4 - 0.042\ T) \pm 1.2$$

Table 4
Heat content of the $x_{Te} = 0.77$ Au-Te alloy (T_0 = 298K) with respect to temperature

T (K)	H(T)-H(298K) (kJ.mol-1)	T (K)	H(T)-H(298K) (kJ.mol-1)
390	2.3	760	30.8
484	4.7	772	31.1
607	8.0	784	31.8
645	8.9	803	32.1
672	9.9	820	33.3
692	16.7	827	33.8
711	20.0	834	33.8
732	29.3	853	34.1
742	30.3	867	34.9
753	30.7	880	35.5

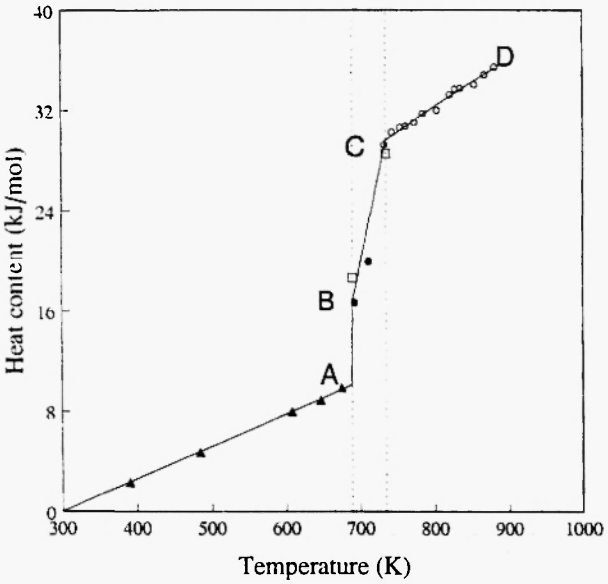

Fig. 4: Heat content of the x_{Te} = 0.77 Au-Te alloy (T_0 = 298K) with respect to temperature. Full triangles: solid state; Open circles: liquid state; Full circles: two-phase domain; Open squares: calculated from the enthalpy of eutetic reaction and the heat content of the solid at 692K (point B) and from the enthalpy of dissolution of the solid in the eutectic and the point B (point C).

3.5. The x_{Te} = 0.667 alloy

Finally, we performed some measurements to check the results of Anres *et al.* /6/ for the $AuTe_2$ compound. The measurements were done just below and above its melting point. The temperature and the enthalpy of melting were found respectively as 737K and 18.6 kJ.mol^{-1} in agreement with the values of Anres *et al.*

4. DISCUSSION AND CONCLUSION

We pointed out in a previous paper /4/ that the enthalpy of mixing of the Au-Te melts undergoes a transition in a narrow temperature range (819-872K) corresponding to an excess Cp of at least 8.7 J.K^{-1}mol^{-1}. Such a transition could obviously yield a jump of the heat content of the liquid alloys in the same range of temperature. However, this jump (~0.45 kJ.mol^{-1}) cannot be observed from our determinations since its value is less than the accuracy of heat content data (33 ± 2 kJ.mol^{-1} at 850K).

One of the thermodynamic functions the most sensible to eventual short-range order is the excess heat capacity. It cannot be calculated here with accuracy for the melts since the heat capacities of pure liquid gold cannot be extrapolated so far from its melting point. Another thermodynamic function sensible to residual short-range order upon melting is $\delta\Delta H = \Delta H^m - \sum x_i \Delta H_i^m$, the difference between the experimental enthalpy of melting, ΔH^m, and the value calculated according to additivity, $\sum x_i \Delta H_i^m$. Such a function can be considered as a rough difference of ordering between the solid and the liquid state.

We found in such a way -6.46 and -7.11 kJ.mol^{-1} for the Ag-Te and Cu-Te eutectics respectively /1/. Such negative values correspond to strong short-range order in the melts in agreement with their negative enthalpies of formation /11,12/. In the investigated temperature range just above the melting point of the alloys, the linear dependences on temperature of the enthalpies of both liquid eutectics lead to constant heat capacities as for many pure liquid metals. There is no drastic change of structure when temperature increases in contrast with the case of the Te-rich Ge-Te eutectic /3/. The enthalpies of mixing of both Ag-Te and Cu-Te systems show strong minima whose locations correspond to their congruently melting compounds (Ag_2Te and Cu_2Te) and the behaviour of both binaries has already been explained in a very simple way by the existence of some Ag_2Te and Cu_2Te species. It can be concluded that these alloys retain their chemical bonding after melting and that the dissociation of the associates takes place at high temperature above their melting points.

The experimental and calculated values of the enthalpy of melting of the five Au-Te alloys are given in Table 5 as well as the data of $\delta\Delta H$ which are positive. It means that there is no residual-short range order after melting. Such behaviour is in agreement with their weakly negative enthalpy of formation and with the low melting point of the intermediate compound when compared to the Ag-Te and Cu-Te alloys.

Table 5

Experimental (column 2), calculated (column 3) and excess (column 4, see text) enthalpies of melting of the Au-Te alloys investigated versus mole fraction of Te.

x_{Te}	ΔH^m(exp) (kJ.mol^{-1})	ΔH(calc) (kJ.mol^{-1})	ΔH (kJ.mol^{-1})
0.53	17.2	17.6	2.0
0.60	17.6	18.2	2.1
0.667	18.6	19.1	2.8
0.77	19.4	18.6	3.0
0.88	17.4	18.2	0.5

REFERENCES

1. S. Louadi, A. Yassin and R. Castanet, *J. Alloys Compounds*, 224, 351 (1995).
2. R. Castanet, *Anales de Fisica*, **86B**, 129 (1990).
3. R. Castanet and C. Bergman, *Phys. Chem. Liquids*, **14**, 219 (1985).
4. A. Yassin and R. Castanet, *J. Alloys Compounds*, **252**, 162 (1997).
5. A. Yassin, R. Chastel and R. Castanet, *Phys. Chem.* Liquids, **34**, 65 (1997).
6. P. Anrès, H. Bros, A. Coulet and R. Castanet, *Phys. Chem. Liquids*, **28**, 63 (1994).
7. H. Okamoto and T.B. Massalski, *Bull. Alloy Phase Diagrams*, **5**, 172 (1984).
8. T. Kang and R. Castanet, *J. Less-Comm. Metals*, **51**, 125 (1977).
9. Certificate of Standard Reference Material 720, Synthetic Sapphire, U.S. Dept. of Commerce, Nat. Bur. Stand., Washington, D.C., U.S.A., 1987.
10. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, Amer. Soc. Met., Metals Park, Ohio, 1973.
11. R. Castanet, Y. Claire and M. Lafitte, *J. Chim. Phys.*, **7-8**, 1133 (1971).
12. R. Castanet and C. Bergman, *J. Chem. Thermodyn.*, **11**, 83 (1979).