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Thermochimica Acta 314 (1998) 265–273

thermochimica acta

The investigation and the thermodynamic analysis of volume properties in HgTe and CdHgTe melts

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Received 6 October 1997; accepted 18 December 1997

Abstract

The temperature dependence of the density in pure HgTe melt and liquid $Cd_xHg_{1-x}Te$ for $x \leq 20$ mol% CdTe has been investigated by the γ-ray attenuation method. The anomalous character of temperature density dependence for the investigated melts should be noted. Both the density and concentration gradient being stable in time have been found by the density measurements along the sample height. This gradient presence can be regarded as a new physical phenomenon in CMT melts (cadmium–mercury–tellurium). The concentration and density gradient formation is being related to the peculiarities of intermolecular interaction nature. The observed change of volume properties in the melts mentioned above has been analyzed on the basis of the associated solution theory. The calculation success in associated model approximation was achieved at the expense of Hg_2Te_3 associate introduction into the model of the chemical structure for these melts. © 1998 Published by Elsevier Science B.V.

Keywords: Mercury telluride; CMT melts; Density; Concentration gradient; Volume properties; Associated solutions

1. Introduction

Our research is devoted to the investigation of volume properties of mercury telluride and cadmium mercury tellurium alloys (CMT) in the liquid phase by the γ-radiation attenuation method [1,2]. These substances are widely used as materials for electronic engineering and are popular objects for experiments on space materials science. Wider use of electronic devices based on CMT is retarded by the difficulties of homogeneous material production. Different techniques are used to solve the question of uniform single bulk crystals, but they have not yet succeeded completely [3,4]. Chemical homogeneous single crystals of solid solution were not obtained even under zero gravity condition, though the attempt to solve the question by this technique is continued.

A small amount of work has been devoted to the study of the temperature dependence of the density of these substances. Negative thermal expansion has been established in pure HgTe melt and liquid $Hg_{1-x}Cd_xTe$ for $x \leq 0.2$ after melting by means of a thermometric method [5–7]. The authors of recent papers [6,7] demonstrated that the observed anomalous effects can be explained using a model based on an extension of the inhomogeneous structure model developed by Cohen and Jortner [8,9].

We studied the temperature dependence of the HgTe density by γ-ray attenuation technique again

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PII S0040-6031(98)00263-9

due to the discrepancy in experimental data [5,6]. The CMT melt volume properties in the same concentration range were investigated by this technique. The method is perspective for the research of the density of inhomogeneous melt. It permitted us to discover new effects in CMT melts, which are discussed below.

2. Experimental procedure

Recently, the densities of HgTe in solid and liquid state and of liquid $Cd_xHg_{1-x}Te$ alloys were measured [10,11]. Synthesis of mercury telluride was performed by direct alloying of pure components. The impurity content in the initial reagents was no more than 10^{-5} wt%. HgTe and CdTe were synthesized to prepare CMT alloys. For the production of crystals of solid solutions the heater travelling method was used [4]. The quality of samples has been controlled using X-ray diffraction, X-ray microscopy and chemical analysis.

The procedure of measuring density by means of penetrating radiation and the construction of the apparatus has been described elsewhere [12]. The sample was placed in an evacuated, sealed quartz container 25 mm i.d. and 60 mm high, which was placed inside a bulk copper block. Temperature was measured by a platinum–platin–rhodium thermocouple embedded into the block wall. Corrections for the difference in temperature between the container and block were determined by special calibration experiments using a sample simulator with an auxiliary thermocouple in the center. Studying the density of melts was mainly carried out in a dynamic mode at heating and cooling rates of no more than 2 K/min. In addition, at some temperatures, the sample density was determined under static conditions after being held 20–30 min at constant temperature.

A specific feature of studying mercury telluride and CMT alloys is that the thermal dissociation of the samples at high temperatures can result in a loss of uniformity and, particularly, in the formation of gas inclusions at the walls of the container. Such defects occur in the zone of γ-quantum beam. Uniformity of a sample was monitored by measurement of the attenuation coefficient of radiation at different heights. This procedure made it possible to locate the defects and avoid their occurrence in the γ-ray zone.

3. Results and discussion

3.1. Mercury telluride

The temperature dependence of the density of mercury telluride in liquid and solid state is shown in Fig. 1. No significant discrepancies were observed for the data obtained under different conditions of measurements. It follows from this figure that at the melting point the change in the density of mercury telluride is of the type, which is observed for water. Earlier density measurements are also given. A comparison indicates that our data for HgTe in the liquid phase coincide, within experimental error, with the data of Regel and Mokrovski [5] and noticeably exceed the data from Chandra and Holland [6,7]. There are two possible reasons for underestimation of densities in both liquid and solid phase. Perhaps, Chandra and Holland did not avoid the gas bubble effect occurring in the melt due to mercury evaporation during the measurements. Moreover, they did not synthesize HgTe *in situ* in a measuring cell. This means that the purity of the sample was not proved both before and after the density measurements. In the present investigation, the purity of the mercury telluride was verified by X-ray diffraction both before and after the density measurements. The measured lattice

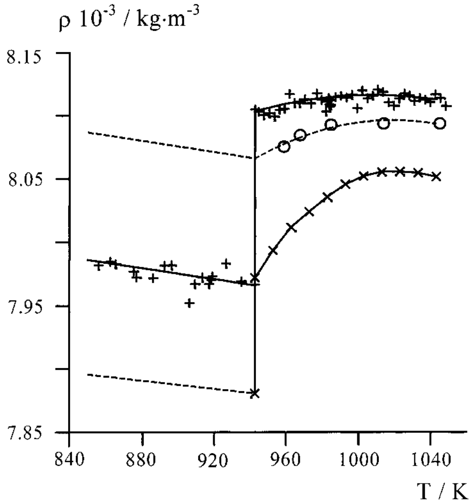

Fig. 1. Density versus temperature for mercury telluride in the vicinity of the crystal-melt phase transition. (O)-data of Regel and Morrovsky [5]; (+)-present results; (×)-data of Chandra and Holland [6,7].

constant coincides with the reference data [13] to the fourth decimal place.

The following analytical expressions for densities of HgTe were obtained by the least-squares fit of the experimental values

$$\rho_S = 8084 \pm 42 - (0.14010 \pm 0.02764)(T - 293) - (6.4187 \pm 4.0167) \cdot 10^{-5}(T - 293)^2,\ \mathrm{kg/m^3} \quad (1)$$

for the solid phase, and

$$\rho_L = 8110.2 \pm 2.6 + (0.52763 \pm 0.07139)(T - 943) - (4.1017 \pm 0.3948) \cdot 10^{-3}(T - 943)^2,\ \mathrm{kg/m^3} \quad (2)$$

for the liquid phase.

Our results indicate unambiguously an increase in density in the course of the solid–liquid phase transition. Hence, the volume effect of the melting of HgTe is negative. This means that, according to the Clausius–Clapeyron equation, increasing the pressure should result in a decrease of the melting temperature. It has been shown in [14,15], that the baric coefficient of the HgTe melting temperature is negative. The volume difference V was determined to be $-1.94{\cdot}10^{-6}$ [14] or $-1.08{\cdot}10^{-6}$ m^3 [15]. Our result of direct determination of the volume effect upon melting of mercury telluride (Fig. 1) gives the value $\Delta V{=}-0.71{\cdot}10^{-6}$m^3. In [6,7], the volume difference has been estimated as $-0.47{\cdot}10^{-6}$ m^3, which is considerably lower than our value. The observed discrepancy between the latter values is caused by a difference in the measured densities of the HgTe melt (Fig. 1), whose reasons were discussed above. Note that the values of the volume effect obtained from the experimental values of the baric coefficient of the melting temperature [14,15] by the Clausius–Clapeyron equation are of the same sign.

The observed abnormal change in density upon heating the melt can be rationalized in terms of the concept of post-melting effect [16,17]. An increase in density of the melt can be caused by an intense decay of clusters that inherit a relatively loose structure of the crystalline phase in the melt immediately after melting. In the temperature range from T_m to T_{max} in the plot of temperature dependence of density, the melt of HgTe can be considered as a two-structural melt.

The quantitative description of the temperature dependence of the HgTe density could also be successfully made on the basis of the associated equilibrium solution theory. It should be noted, that according to Chandra's [7] opinion, the observed anomaly of the temperature dependence of the specific volume could not be satisfactorily explained by means of models based upon the dissociation of mercury monotelluride. We suggest a chemical structure model of the HgTe melt including the HgTe associate the possibility of more complex Hg_2Te_3 associates. This probability is shown by the presence of the minimum on the curve of the concentration dependence of excess entropy of mixing of Hg–Te liquid alloys [18] at the composition of Hg_2Te_3. In the HgTe melt the following chemical processes related to thermal dissociation of suggested associates:

$$Hg_2Te_3 = 2HgTe + Te \quad (3)$$

$$HgTe = Hg + Te \quad (4)$$

can take place.

The enthalpies and entropies of reactions (1) and (2) were found by fitting calculated and experimental partial pressures of Hg and Te_2 along with the three-phase line HgTe(c). In the Section 2, experimental data of Brebrick and Strauss work [19] obtained by the optical density measurement technique were used (see Table 1).

These data permitted us to evaluate the change of mole fractions of associates and monomers in HgTe with temperature increase Fig. 2. Using the associate and monomer distribution at every given temperature the temperature dependence of the molar volume in the approximation can be calculated by equation

$$V = \frac{(x_{Hg} \cdot V^0_{Hg} + x_{Te} \cdot V^0_{Te} + x_{HgTe} \cdot V^0_{HgTe} + x_{Hg_2Te_3})}{(1 + x_{HgTe} + 4x_{Hg_2Te_3})} \quad (5)$$

Table 1
Values of thermodynamic parameters for reaction (3) and (4), calculated from (p–T)-diagrams for Hg(g) and Te_2(g) [19]

Associate	$\Delta_r H$ (kJ·mol^{-1})	$\Delta_r S$ (kJ·mol^{-1}·K^{-1})
HgTe	40.13	28.5
Hg_2Te_3	131.3	136.6

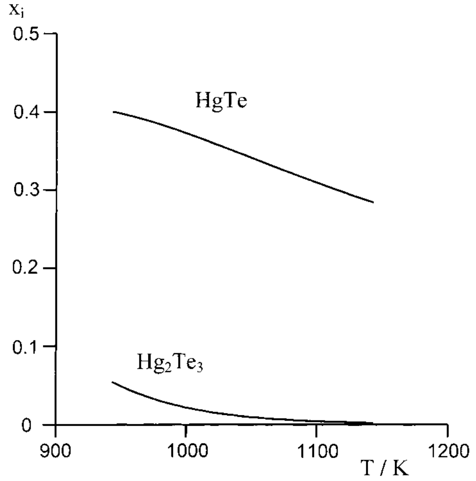

Fig. 2. Mole fractions HgTe and Hg_2Te_3 associates versus temperature in HgTe melt.

The molar volumes of associates and monomers in the HgTe melt are temperature dependent. This dependence is expressed by

$$V_i^0(T) = V_i^0(T_m)[1 + \alpha_i(T - T_m)], \qquad (6)$$

T_m is the melting temperature of HgTe, α_i is the thermal expansion coefficient of component i of the melt under study (i=0 or 1).

$V_i^0(T)$ and α_i at the melting temperature of HgTe for monomers were taken such as for elements Hg and Te from [20,21]. The same parameters for HgTe and Hg_2Te_3 associates were obtained by fitting calculated values of molar HgTe melt volumes to experimental ones (Fig. 3) as it was done in the two-structural model parameter definition.

The temperature dependence of the specific volume of the HgTe melt is given in Fig. 3. It is seen that the curve calculated in accordance with the association equilibrium theory is in very good agreement with the experimental data obtained by the γ-ray attenuation technique [12]. The complex structure of the HgTe melt is confirmed by neutron diffraction conducted by Gaspard et al. [22]. According to their data the structural factor for HgTe melt has a characteristic shoulder which is the evidence of the loosely-structured clusters predominatingly with covalent interatomic bonds.

3.2. *Cadmium mercury telluride alloys*

A new effect was detected when investigating the temperature dependence of the density of $Cd_xHg_{1-x}Te$ melts containing less than 20 mol% of CdTe in addition to the HgTe anomaly described above. While investigating the temperature dependence of the densities of molten $Cd_xHg_{1-x}Te$ with CdTe contents up to 20 mol%, we discovered a density gradient in the height which is related to a CdTe concentration gradient.

In the γ-technique, direct measurements of a series of μ and ρ values were made, where μ is the mass coefficient of radiation attenuation and ρ the density of the sample. Both parameters correspond to a point of the path of the gamma-quantum beam. The value of μ was estimated as follows:

$$\mu = \mu_{CdTe}(x) + \mu_{HgTe}(1 - x), \qquad (7)$$

where x is the mole fraction of CdTe, and μ_{CdTe} and μ_{HgTe} are the mass coefficients of radiation attenuation of each component determined separately. When a concentration gradient $x(h)$ takes place in the melt, the values of μ and ρ must change along the samples height,

$$\mu \cdot \rho = f(h) \qquad (8)$$

where h is the height of the gamma-ray beam above the bottom of the samples container. For example, the observed concentration gradient in liquid $Hg_{0.808}Cd_{0.192}Te$ along the samples height is shown in Fig. 4. Similar results were obtained when investigating the density of melts having 0.05, 0.10 and 0.15 mol fractions of CdTe. Within experimental errors the dependencies $x=f(h)$ in Fig. 4 are linear, and the slope of the straight line slowly decreases with time. The intersection of the straight lines (isochrones) is around the point h_0, i.e. at a height corresponding to about a half of the samples height. In the vicinity of this point, $\mu \cdot \rho$=const, i.e. the composition in the middle of the sample does not change with time, and, evidently, equals the mean composition x_0 of the sample. The leveling-up of the composition with time observed in these experiments is related to diffusion, because convection is not expected due to isothermal conditions under which the measuring cell was held. Note that in other melts under study the concentration gradient and density change, respec-

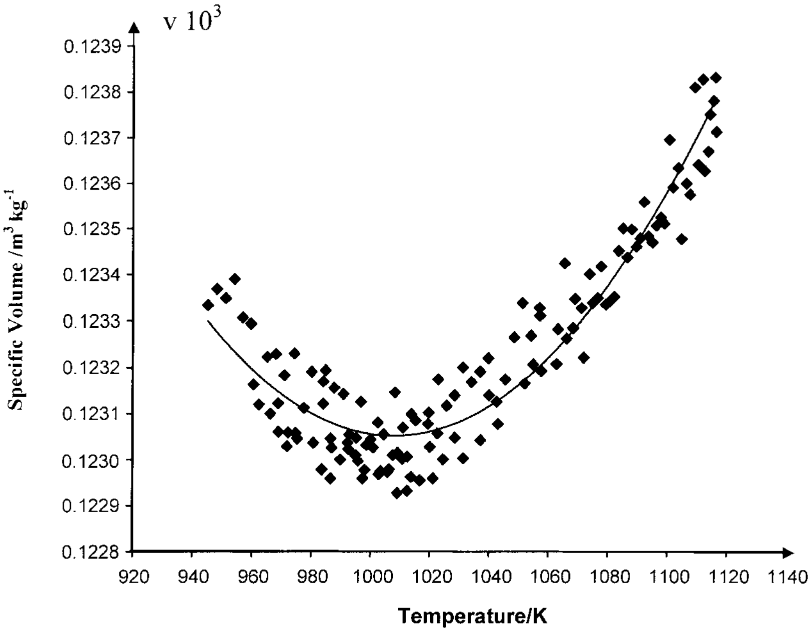

Fig. 3. The temperature dependence of the specific volume of molten HgTe: circles are our experimental data, solid line represents our calculation by the associated solution model.

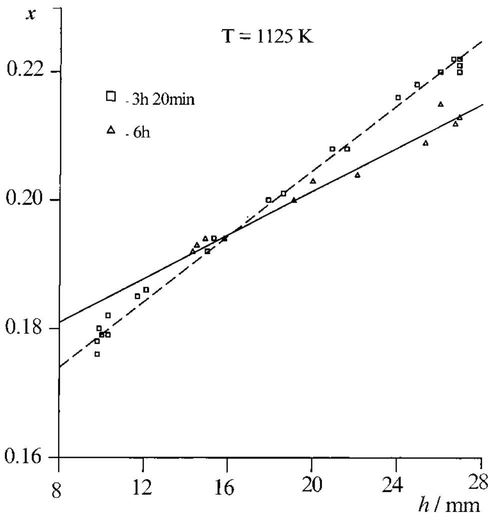

Fig. 4. The concentration profiles change along the height of the sample at different time intervals after melting of $Cd_{0.1}Hg_{0.9}Te$.

tively, with time practically do not occur (within the time limits of 3–5 h). The observed effect considerably exceeds the measurement error limits and can be considered as a new phenomenon in alloys of systems with unlimited solubility in both solid and liquid solutions.

To determine the density it is not required that the sample composition is uniform with height. It is sufficient to make measurements at the height of the gamma beam equal to h_0, i.e. where the composition does not change with time. Fig. 5 shows our results for the temperature dependence of $Cd_xHg_{1-x}Te$ melt density and compares them with the previous data [6,7]. Our measurements and these results coincide within the limit of experimental error for compositions with x=0.1 and close to x=0.2, but they are noticeably different for $Hg_{0.95}Cd_{0.05}Te$ melt. The different behavior of the density for the investigated alloys should be noted. For alloys with a small CdTe content the density changes along a curves with maximum while for the alloy with 0.192 mol fraction of CdTe the density linearly decreases within the experimental errors.

The obtained experimental data were treated by least-squares method. As a result of the following approximated equations of the temperature dependence of the density of the liquid CMT alloys were obtained:

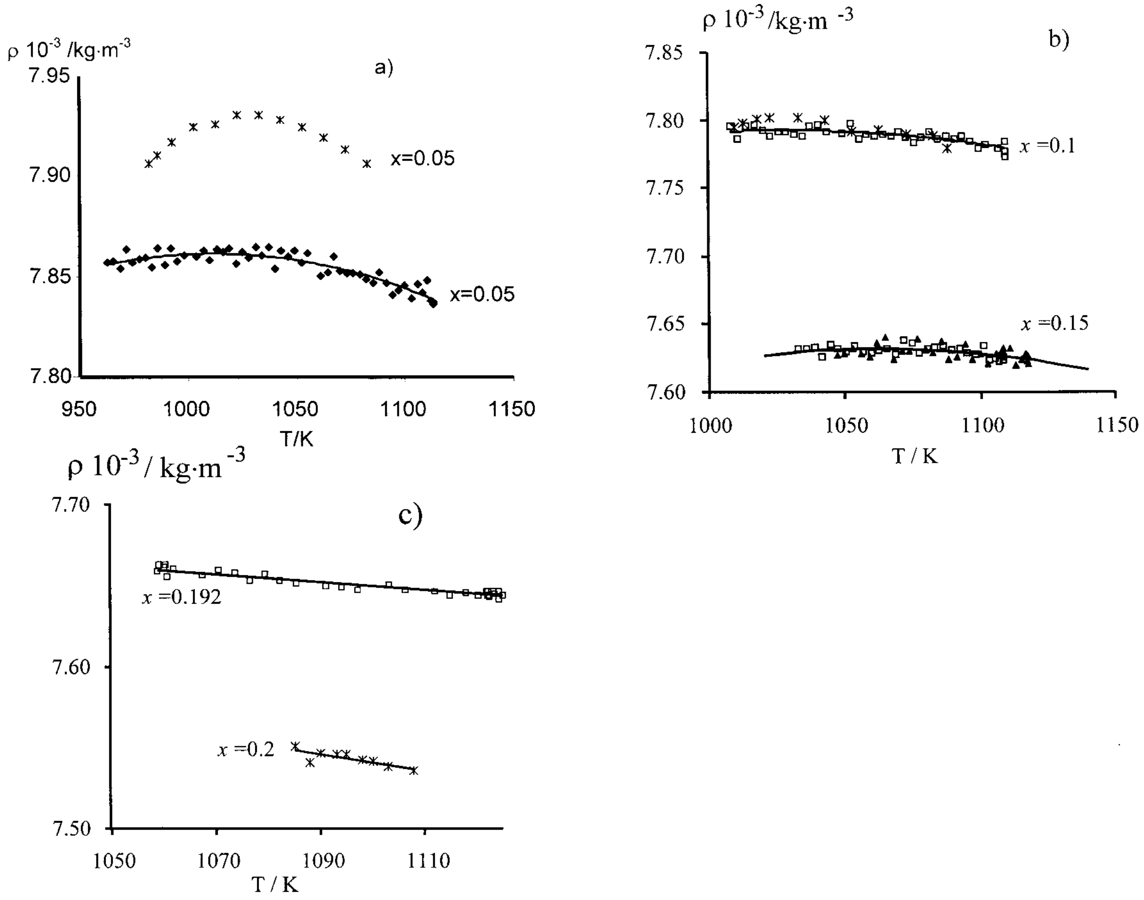

Fig. 5. The temperature dependence of density for $Cd_xHg_{1-x}Te$: (*) data of Chandra and Holland [6,7], our results:(◆) (□) - cooling I, (▲) - cooling II.

$$\rho_l = (7779.3 \pm 2.3) - (0.44545 \pm 0.07139) \cdot (T - 1113.1) - (2.2010 \pm 0.4966) \cdot 10^{-3} \cdot (T - 1113.1)^2,\ \mathrm{kg/m^3} \quad \text{for } Cd_{0.05}Hg_{0.95}Te \tag{9}$$

$$\rho_l = (7790.8 \pm 4) + (0.1141 \pm 0.17 \cdot 10^{-5}) \cdot (T - 1001) - (2.02336 \pm 1.4 \cdot 10^{-7})10^{-3} (T - 1001)^2,\ \mathrm{kg/m^3} \quad \text{for } Cd_{0.1}Hg_{0.9}Te \tag{10}$$

$$\rho_l = (7624.0 \pm 2.4) - (0.28706 \pm 0.15346) (T - 1117.3)^2 - (2.6483 \pm 1.9281)10^{-3} \cdot (T - 1117.3)^2, \mathrm{kg/m^3} \quad \text{for } Cd_{0.15}Hg_{0.85}Te \tag{11}$$

$$\rho_l = (7659.1 \pm 1.3) - (0.2488 \pm 0.029) (T - 1061),\ \mathrm{kg/m^3} \quad \text{for } Cd_{0.192}Hg_{0.808}Te \tag{12}$$

The physical reasons causing the anomalous change of density with temperature for CMT alloys containing less than 0.192 mol fraction CdTe are the same as for pure HgTe (see [6,7,10]), namely a post-melting effect [16,17] observed for quasi-binary alloys, i.e. for the specimens of complex chemical composition in comparison with simple substances and individual chemical compounds.

Below we shall discuss the concentration dependence of molar volume and thermal expansion coefficient in HgTe–CdTe quasi-binary system under study. The analysis shows that the alloy containing

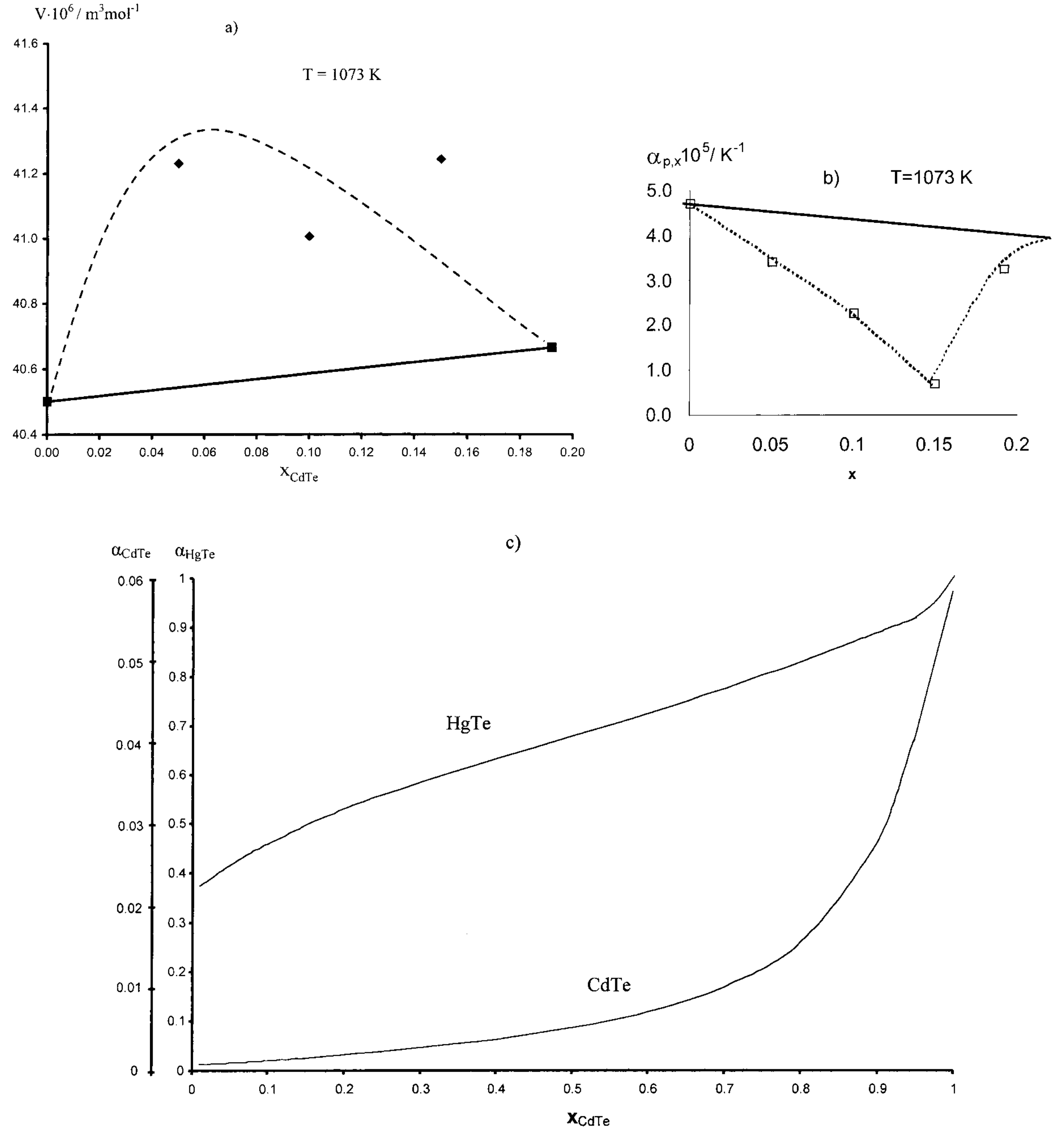

Fig. 6. The concentration dependencies of molar volume (a), thermal expansion coefficient (b), and the HgTe and CdTe dissociation degree (c), along the liquidus curve in the HgTe–CdTe quasi-binary system.

0.192 mol fraction of CdTe has a molar volume at 1073 K according to Vegards rule (See Fig. 6(a)). For the alloys with 0.05; 0.10; 0.15 mol fraction of CdTe, the values of the specific volume of the melt obtained at this temperature considerably deviate from the additive line to higher values. The thermal expansion coefficient of the investigated melts shows a sharp minimum at 0.15 mol fraction CdTe (see Fig. 6(a)(b)).

It should be noted that a change in the liquidus curve slope of the HgTe–CdTe quasi-binary system corresponds to the same concentration [23]. Both the HgTe and CdTe dissociation degree were calculated by the approximation of ideal associated solutions by methods described in our previous work [24]. In case of HgTe melt the presence of two associates (HgTe and Hg_2Te_3) has been taking into account as mentioned above. CdTe dissociation in the liquid state occurs according

$$\mathrm{CdTe} = \mathrm{Cd} + \mathrm{Te} \tag{13}$$

The HgTe dissociation increases noticeably in the investigated composition range while the CdTe dissociation is quite small (Fig. 6(c))

The calculation of the partial vapor pressure of the mercury along the liquidus curve of HgTe–CdTe diagram performed with these assumptions is presented in Fig. 7 in comparison with data of Yu and Brebrick [25]. The curves have identical slopes, but their values differ slightly at all compositions.

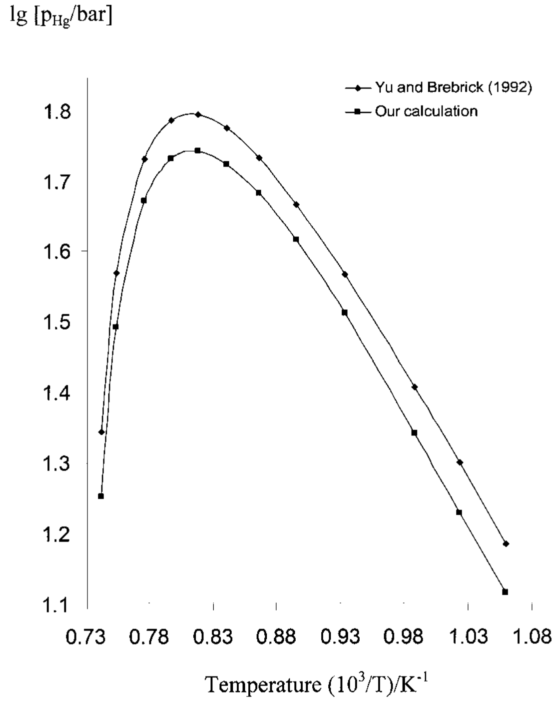

Fig. 7. Comparison of Hg(g) vapor pressures calculated by the associated solution model with fitted experimental data [25] for liquid HgTe–CdTe alloys.

The deviations of CMT melt volume properties from Vegards rule in the investigated concentration range may be connected with the presence of clusters with looser atom packing. It can be supposed that the positive deviation from the additivity for these alloys are related with the presence of associates promoting the formation of looser structured components in comparison with those for pure HgTe and CdTe. The formation of more complex associates can be supposed including polyanions, which are built from Hg_2Te_3 five membered rings.

Four polyanions have been synthesized and have been structurally characterized [26]. They are $Hg_2Te_4^{2-}$-, $Hg_2Te_5^{2-}$, $Hg_3Te_7^{4-}$ and $Hg_4Te_{12}^{4-}$. It can be supposed that Hg_2Te_3 associates interact possibly with strongly polarized CdTe associates. As a result $Hg_2Te_4^{2-}$ polyanion formation might be possible, the charge of which is neutralized by the cadmium ion. Finally the complex $[Cd^{2+}(Hg_2Te_4)^{2-}]$ is formed.

4. Conclusion

The reasons of the density gradient and concentration occurring in $Cd_xHg_{1-x}Te$ melts are the formation of complex polyanions on Hg_2Te_3 basis according to our hypothesis. The results of [26] confirm the possibilities of such polyanion formation derived from HgTe-alloys.

References

[1] P.M. Nash, S.G. Steinemann, Phys. Chem. Liq. 29 (1995) 43.
[2] V.M. Glazov, M. Vobs, V.I. Timoshenko, Metody issledovaniya svoistv zhidkih metallov i poluprovodnikov, Metallurgiya, Moscow, 1989.
[3] V.N. Romanenko, Upravlenie sostavom poluporvodnikovyh sloev, Metallurgiya, Moscow, 1978.
[4] I.B. Mizetskaya, G.S. Oleynik, L.D. Budennaya, V.N. Tomashik, I.D Oleynik, Fiziko-khimicheskie osnovy sinteza monokristallov poluprovodnikovyh tverdyh rastvorov soedinenii A^2B^6, Naukova Dumka, Kiev, 1986.
[5] N.P. Mokrovski, A.R. Regel, Zhurnal tehnicheskoi fiziki 22 (1952) 1281.
[6] D. Chandra, L.R. Holland, J. Vac. Sci. Technol. A 1 (1983) 1620.
[7] D. Chandra, Phys. Rev. B 31 (1985) 7206.
[8] M.H. Cohen, J. Jortner, Phys. Rev. A 10 (1974) 978.
[9] J. Jortner, M.H. Cohen, Phys. Rev. B 13 (1976) 1548.

[10] V.M. Glazov, L.M. Pavlova, S.V. Stankus, R.A. Khairulin, Dokl. Akademii nauk 347 (1996) 202.
[11] V.M. Glazov, L.M. Pavlova, S.V. Stankus, R.A. Khairulin, Dokl. Akademii nauk 354 (1997) 207.
[12] S. V Stankus, R.A. Khairulin, Teplofizika vysokih temperatur 30 (1992) 487.
[13] Fiziko-khimicheskie svoistva poluprpvod- nikovyh veschestv, Spravotchnik pod redaktsiei, A.V. Novoselovoi, V.B. Lazareva, Nauka, Moscow, 1979.
[14] J.C. Tedenac, M.C. Record, R.M. Ayral, G Brun, J Jun, I. Grzegory, S. Krukowski, M. Bockowskii, Jap. J. Appl. Phys. 32 (1993) 26.
[15] A.V. Omel′ chenko, V.I. Soshnikov, Izvestiya AN SSSR. Neorganitcheskie materialy 18 (1982) 685.
[16] A.R. Regel, V.M. Glazov, Zakonomernosti formirovaniya struktury elektronnyh rasplavov Nauka, Moscow, 1982.
[17] A.R Regel, V.M. Glazov, Fizika i tehnika poluprovodnikov 17 (1983) 1729.
[18] A. Marbeuf, M. Ferah, E. Janik, A. Heurtel, J. Cryst. Growth 72 (1985) 126.
[19] R.F. Brebrick, A.J. Strauss, J. Phys. Chem. Solids 26 (1965) 989.
[20] V.I.Nizhenko, In: Metody issledovaniya i svoistva granitz razdela konkurirujuschikh faz, Naukova Dumka, Kiev, 1977, p. 125.
[21] A.R.Regel′, V.M. Glazov, Fizicheskie svoistva elektronnykh rasplavov, Nauka, Moscow, 1980.
[22] J.P. Gaspard, J.Y. Raty, R. Ceolin, R. Bellissent, Proceedings of LAM9 conference (Chicago, Aug. 1995).
[23] J. Yang, N.J. Silk, A. Watson, A.W. Bryant, T.G. Chart, B.B. Argent, CALPHAD 19 (1995) 415.
[24] V.M. Glazov, L.M. Pavlova, Khimicheskay Termodinamika, Metallurgya, Moscow, 1989.
[25] T.-C. Yu, R.F. Brebrick, J. Phase Equilibria 13 (1992) 476.
[26] S.S. Dhingra, Ch.J. Warren, R.C. Haushalter, A.B. Bocarsly, Chem. Mater. 6 (1994) 2382.