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Molar heat capacities of CdTe, HgTe and CdTe–HgTe alloys in the solid state

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Abstract

Using a differential scanning calorimeter, the molar heat capacities of the two components HgTe and CdTe and of ten solid alloys of the CdTe–HgTe system were measured at constant pressure between 300 K and 523 K.

Irregular variations of the $C_p = f(T)$ curves of CdTe–HgTe alloys suggest the existence of a solid state miscibility gap in this system. The limit of the (solid$\leftrightarrow$solid$_{(1)}$+solid$_{(2)}$) miscibility gap and coordinates of the critical temperature ($x_{CdTe} = 0.55$, $T = 455$ K) are proposed.

From C_p data obtained in a single-phase solid region, the excess molar heat capacities ($\Delta C_p = C_{p(exp)} - C_{p(calc)}$) at 500 K were deduced: the maximum negative excess C_p is located at $x_{CdTe} = 0.5$.

1. Introduction

The study of variations of thermodynamic properties of a system in the vicinity of critical points is of particular interest in investigations of the equilibrium phase diagram: n-order phase transitions are characterized by singularities in some thermodynamic functions at critical points and along critical lines or surfaces (a first-order transition is characterized by a discontinuous first derivative, $V = f(T)$ or $H = f(T)$, of the chemical potential μ whereas, in a second-order phase transition, the first derivative is continuous but the second derivative is discontinuous, $C_p = f(T)$ for instance).

These thermodynamic considerations can explain the difficulties encountered in obtaining a precise delimitation of miscibility gaps using classical experimental methods (thermal analysis, differential thermal analysis, X-ray diffraction, visual method, ...). In contrast, for n-component mixtures,

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measurements of the molar heat capacity *vs.* temperature and molar fraction allow the coordinates of phase equilibria (liquid ↔ liquid 1 + liquid 2 or $\text{solid} \leftrightarrow \text{solid}_{(1)} + \text{solid}_{(2)}$) to be determined with good accuracy.

With the recent progress achieved in differential scanning calorimetry, it seems quite natural to employ this technique to determine C_p values of multicomponent systems with varying composition over large temperature ranges to detect the critical lines.

Using a differential scanning calorimeter, C_p values *vs.* temperature of CdTe–HgTe solid alloys were measured. Much has been published about the CdTe–HgTe system; we will not report the thermodynamic data here in detail, but we recall that the equilibrium phase diagram is of the simplest type: HgTe and CdTe form a complete series of solid solutions which have the ZnS structure. The mercury and cadmium atoms are randomly distributed over the sites of one sublattice. Among the many thermodynamic data published, the heat capacities of CdTe–HgTe alloys are missing. Unfortunately, for a better assessment of the phase diagram, the values of molar heat capacities of the components and alloys *vs.* temperature are required.

At temperatures ranging from 303 K to 523 K, the $C_p = f(T)$ curves of alloys were obtained and some of them (with $0.253 \leqslant x_{\text{CdTe}} \leqslant 0.800$) exhibited an irregular shape. From considerations of these irregularities in the molar heat capacities, we suggest the existence of a large miscibility gap in the solid state.

2. Experimental details

2.1. *Alloy preparation and analysis*

2.1.1. *Preparation*

Known masses of tellurium, cadmium (powder) and mercury of high purity (99.999 at.%) were placed in quartz crucibles (10 mm in diameter), sealed under vacuum (10^{-3} Pa) and heated at 673 K. Every 3 h, the temperature of the furnace was increased by 50 K. At 723 K, the temperature was stabilized for one week then slowly decreased over one day. The ingots obtained were ground. Using a special mould, pellets were prepared (14 mm in diameter, 10 mm high). These pellets were maintained under vacuum in sealed ampoules at 723 K for one week, and then slowly cooled to 423 K.

2.1.2. *Analysis*

All alloys were analysed by X-ray diffraction using Cu Kα radiation with a DRON apparatus. The variation of the lattice parameter a(Å) of the CdTe–HgTe solid solutions follows Vegard's law and is given by:

$$a = 6.4637 + 2.02 \times 10^{-2} x_{\text{CdTe}} \qquad (1)$$

with standard deviation $2S_0 = \pm 0.002$ Å

2.2. *Calorimetric measurements*

The experimental method used to determine the molar heat capacity of several materials has been described elsewhere [1–3].

2.2.1. *Principle*

Ideally, the molar heat capacities should be determined using an adiabatic calorimeter, but recent technical progress in differential scanning calorimetry allows variations of C_p with temperature to be obtained over large temperature ranges.

The specific heat of a sample is calculated from the relationship

$$C_p = (dH/dT)_p$$

and if $T=f(t)$ $C_p = ((dH/dt)/(dT/dt))_p$

then $(dH/dt)_p = C_p(dT/dt)_p \qquad (2)$

where H, T and t are respectively enthalpy, temperature and time.

If the temperature increases from T_1 to T_2 during the period $t_2 - t_1$, eqn. (1) may be written

$$\int_{t_1}^{t_2} (dH/dt)_p = \int_{t_1}^{t_2} C_p(dT/dt)$$

with the assumption that the heat capacity is constant for a narrow temperature range, then

$$C_p = [H]_{t_1}^{t_2}/[T]_{t_1}^{t_2}$$

Consequently, the practical determination of $C_p = f(T)$ with a differential scanning calorimeter demands knowledge of the increase in temperature of the calorimeter containing the experimental and reference cells and measurement of the variation in enthalpy during the same period.

2.2.2. *Apparatus*

The apparatus used in this work (DSC 111, Setaram Co.) is designed as a Calvet calorimeter: two cylindrical cells, reference and laboratory cells, surrounded by thermal fluxmeters are located in a metallic block, the temperature of which can be linearly programmed. The two fluxmeters are connected with opposite signs. From observation of the thermal disequilibrium between the two cells during a heat pulse, the heat capacity of the sample contained in the laboratory cell can be obtained as a function of the temperature. The reference cell contains an inert material (alumina for example). It should be emphasized that two calibration methods were employed: in one method, a standard N.I.S.T. (National Institute of Standards and Technology) alumina crystal was used for comparison and, in the other, direct Joule heating of an electrical resistance located in the cell was used. This apparatus can be operated between 173 K and 1023 K.

Consequently, in measuring heat capacities, the following procedure was adopted under the same experimental conditions (constant heat rate, identical temperature range, identical argon flow, ...).

(i) The "zero test", with two identical empty containers, allows the thermal disequilibrium between the reference and laboratory cells to be determined.

TABLE 1

Molar heat capacity of CdTe and HgTe between 300 and 523 K

T (K)	HgTe		CdTe	
	$C_{p(exp)}$ (J K^{-1} mol^{-1})	$C_{p(calc)}$ (J K^{-1} mol^{-1})	$C_{p(exp)}$ (J K^{-1} mol^{-1})	$C_{p(calc)}$ (J K^{-1} mol^{-1})
303	26.60	26.68	25.60	25.65
308	26.64	26.70	25.83	25.68
313	26.75	26.72	25.66	25.70
318	26.78	26.74	25.70	25.73
323	26.81	26.76	25.69	25.76
328	26.91	26.78	25.96	25.79
333	26.98	26.80	25.91	25.82
338	26.91	26.82	25.91	25.85
343	26.70	26.84	26.06	25.88
348	26.98	26.86	26.11	25.91
353	26.86	26.88	26.11	25.94
358	26.81	26.90	26.01	25.96
363	26.71	26.92	25.86	25.99
368	26.85	26.94	26.11	26.02
373	26.95	26.96	26.06	26.05
378	26.80	26.98	26.06	26.08
383	27.04	27.00	25.91	26.11
388	27.04	27.02	25.96	26.14
393	26.88	27.04	26.06	26.17
398	27.00	27.06	26.01	26.19
403	27.07	27.08	26.06	26.22
408	27.16	27.10	26.21	26.25
413	27.23	27.13	26.31	26.28
418	27.20	27.15	26.21	26.31
423	27.27	27.17	26.01	26.34
428	27.30	27.19	26.21	26.37
433	27.31	27.21	26.36	26.40
438	27.23	27.23	26.41	26.42
443	27.20	27.25	26.46	26.45
448	27.33	27.27	26.51	26.48
453	27.26	27.29	26.61	26.51
458	27.19	27.31	26.61	26.54
463	27.26	27.33	26.46	26.57
468	27.33	27.35	26.46	26.60
473	27.36	27.37	26.66	26.63
478	27.54	27.39	26.71	26.66
483	27.48	27.41	26.71	26.68
488	27.52	27.43	26.96	26.71
493	27.48	27.45	26.81	26.74
498	27.56	27.47	26.91	26.77
503	27.41	27.49	26.86	26.80
508	27.41	27.51	26.86	26.83
513	27.50	27.53	26.91	26.86
518	27.48	27.55	26.86	26.89
523	27.56	27.57	26.91	26.91

$C_{p(exp)}$, this work; $C_{p(calc)}$ smoothed values.

(ii) The "experimental test" is performed with the sample in the experimental cell.

(iii) The "calibration test" is performed using either the Joule effect or a well known mass of standard N.I.S.T. alumina crystal. The discrepancy between our experimental results and the reference data (N.I.S.T.) was always less than 0.5%.

Great care has to be taken in protecting the samples in the cell: alloys (about 200 mg) were placed in gas-tight stainless crucibles (6 mm diameter by 20 mm length) and all experiments were performed under purified argon flow. Over the temperature range 300–523 K, the heat capacity of the sample was determined every 5 K. The heating rate was 1.5 K min^{-1} for 200 s and the temperature was maintained constant for 400 s.

Temperatures were determined at ± 0.5 °C and molar heat capacities were measured with an accuracy of about 2%.

3. Results

Over the temperature range 303–523 K, the molar heat capacities of CdTe, HgTe and of ten HgTe–CdTe alloys (with $x_{\text{CdTe}} = 0.0996$, 0.118, 0.253, 0.350, 0.400, 0.500, 0.544, 0.600, 0.700 and 0.800) were determined.

3.1. Molar heat capacity of CdTe and HgTe

The molar heat capacity of these two compounds (CdTe and HgTe) may be expressed (in joules per kelvin per mole) as

$$C_{\text{p, CdTe}} = 23.90_2 + 0.00576T \tag{3}$$

$$C_{\text{p, HgTe}} = 25.44_5 + 0.00406_8T \tag{4}$$

Table 1 and Fig. 1 show experimental and smoothed data for $C_{\text{p, CdTe}}$; good agreement is found with values obtained using the Neumann–Kopp rule. The heat capacities of the elements (tellurium and cadmium) are from Hultgren *et al.* [4].

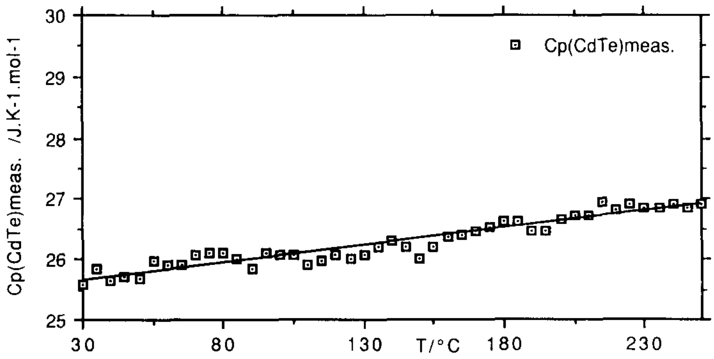

Fig. 1. Molar heat capacity of CdTe *vs.* temperature; ——, experimental results from eqn. (3).

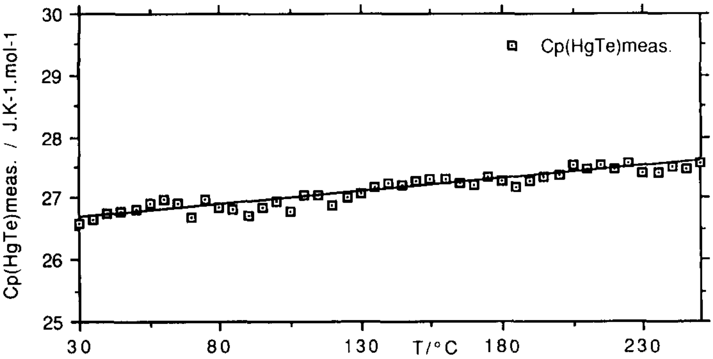

Fig. 2. Molar heat capacity of HgTe *vs.* temperature; ——, experimental results from eqn. (4).

TABLE 2

Molar heat capacities of CdTe and HgTe

CdTe

T (K)	C_p (J K^{-1} mol^{-1}) This work	Ref. 5	Ref. 5 compilation
360	25.98	25.91	25.67
380	26.10	25.91	25.80
400	26.21	25.78	25.93
420	26.32	25.89	26.07
440	26.44	25.98	26.20
460	26.55	26.02	26.34
480	26.67	25.90	26.48
500	26.78	25.99	26.62
520	26.90	26.22	26.76

HgTe

T (K)	C_p (J K^{-1} mol^{-1}) This work	Ref. 6 experimental	Ref. 6 estimated
293	26.64	26.78	26.13
333	26.80	26.67	26.91
373	26.96	26.68	26.84
413	27.13	26.78	26.87
453	27.29	26.85	26.94
503	27.49	27.12	27.07

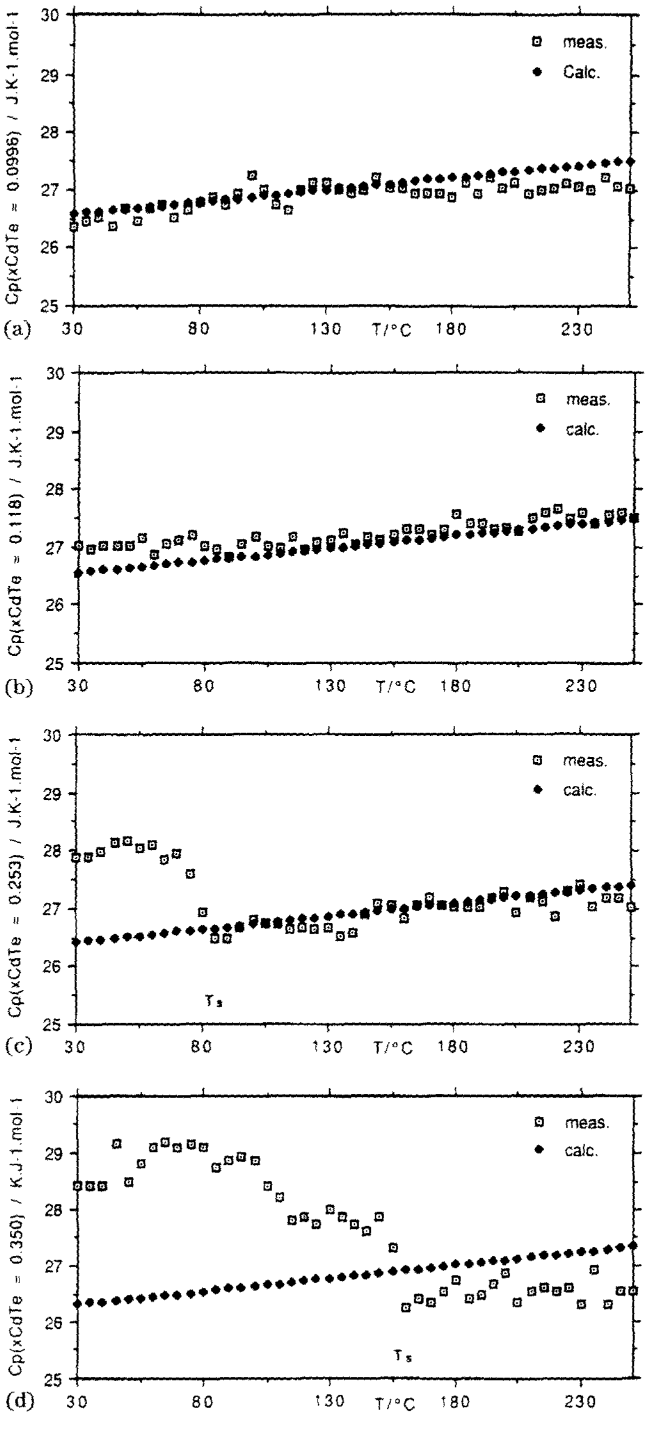

Fig. 3. *(continued)*

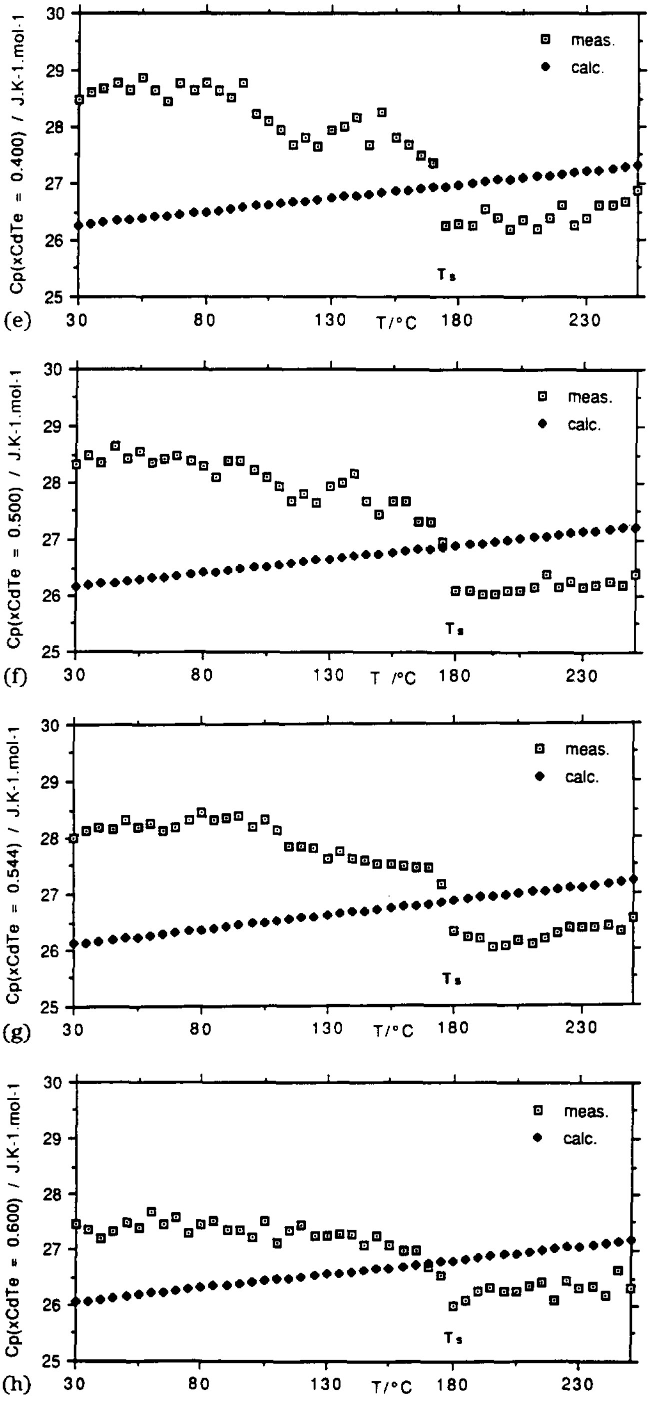

Fig. 3. *(continued)*

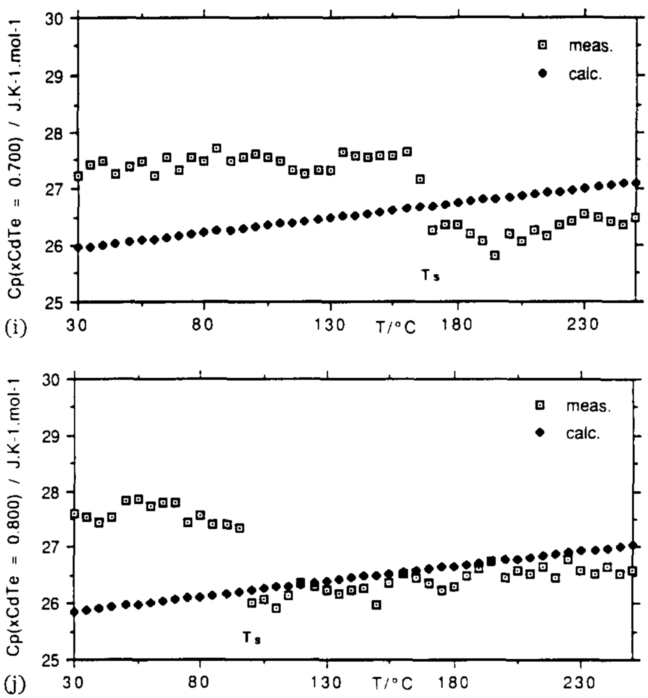

Fig. 3. Molar heat capacity of CdTe–HgTe alloys *vs.* temperature; □ experimental results, ◆ values calculated using eqns. (3) and (4) and the Neumann–Kopp rule: (a) $x_{\mathrm{CdTe}}=0.0996$; (b) $x_{\mathrm{CdTe}}=0.118$; (c) $x_{\mathrm{CdTe}}=0.253$; (d) $x_{\mathrm{CdTe}}=0.350$; (e) $x_{\mathrm{CdTe}}=0.400$; (f) $x_{\mathrm{CdTe}}=0.500$; (g) $x_{\mathrm{CdTe}}=0.544$; (h) $x_{\mathrm{CdTe}}=0.600$; (i) $x_{\mathrm{CdTe}}=0.700$; (j) $x_{\mathrm{CdTe}}=0.800$.

Experimental results for HgTe are gathered in Table 1 and Fig. 2.

Table 2 allows these results to be compared with those carried out by Malkova [5] and Kelemen *et al.* [6] for CdTe and HgTe. After compilation the following relation was proposed by Malkova ($C_{\mathrm{p,\,CdTe}}$ in joules per kelvin per mole)

$$C_{\mathrm{p,\,CdTe}}=22.980+7.170\times10^{-3}T+13633.5T^{-2}$$

3.2. *Molar heat capacity of CdTe–HgTe alloys*

The experimental values of C_{p} for the CdTe–HgTe system are reported in Fig. 3(a)–(j). Using eqns. (3) and (4) and the Neumann–Kopp rule, the molar heat capacities were calculated.

From these results, the following may be noted.

(i) If $x_{\mathrm{CdTe}}<0.253$, the $C_{\mathrm{p}}=f(T)$ law is quasi-linear and reasonably reliable estimates are obtained with the Neumann–Kopp rule (Fig. 3(a), (b)).

(ii) If $x_{\mathrm{CdTe}}>0.253$, $C_{\mathrm{p}}=f(T)$ plots (Fig. 3(c)–(j)) exhibit a step at temperature T_{s} with a linear variation of C_{p} if $T>T_{\mathrm{s}}$. Below the temperature of the step, the variation of C_{p} is irregular and $\Delta C_{\mathrm{p}}=C_{\mathrm{p(exp)}}-C_{\mathrm{p(calc)}}$ values are large and positive. Up to T_{s}, the calculated (using the Neumann–Kopp rule) and experimental values are in good agreement.

Comparing the $C_p = f(T)$ curves obtained for all these alloys, it can be concluded that T_s corresponds to the appearance of an equilibrium in the solid state, for example solid ↔ $\text{solid}_{(1)} + \text{solid}_{(2)}$. The shape of the solid miscibility gap is shown in Fig. 4.

The large value of ΔC_p may be due to the presence of two phases and to the thermal effect associated with the change in equilibrium (solid ↔ $\text{solid}_{(1)} + \text{solid}_{(2)}$) during heating (from T_1 to T_2) of the C_p measurement. Table 3 shows values of T_s and x_{CdTe}. These results will be confirmed by analysis of e.m.f. measurements performed with these alloys over the same temperature range [7].

From the values gathered in Table 3, the equation of the miscibility gap was deduced (with $x \equiv x_{\text{CdTe}}$, T in kelvins):

$$T = -557.11 + 7216.9x - 1.9603 \times 10^4 x^2 + 2.4090 \times 10^4 x^3 - 1.1306 \times 10^4 x^4$$

with 300 K $< T <$ 455 K. The coordinates of the critical point are $x_{\text{CdTe}} = 0.55$ and $T = 455$ K.

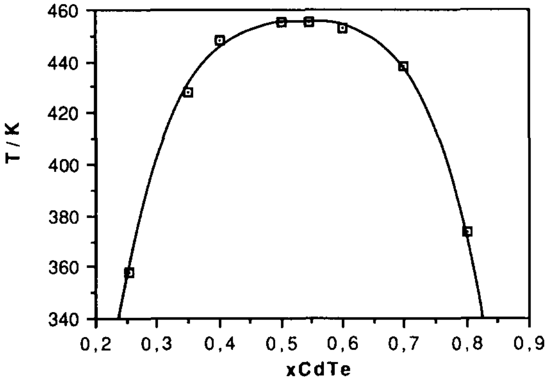

Fig. 4. Miscibility gap of the solid CdTe–HgTe system.

TABLE 3

$C_p = f(T)$ equations obtained in the single-phase region of the solid CdTe–HgTe system

x_{CdTe}	C_p (J K^{-1} mol^{-1})	Temperature range (K)	T_{equ} (K)
0.253	$C_p = 25.137 + 4.068 \times 10^{-3} T$	358–523	358
0.350	$C_p = 25.874 + 1.389 \times 10^{-3} T$	428–523	428
0.400	$C_p = 23.585 + 5.859 \times 10^{-3} T$	448–523	448
0.500	$C_p = 24.407 + 3.614 \times 10^{-3} T$	455–523	455
0.544	$C_p = 24.014 + 4.621 \times 10^{-3} T$	455–523	455
0.600	$C_p = 24.317 + 4.050 \times 10^{-3} T$	453–523	453
0.700	$C_p = 24.521 + 3.657 \times 10^{-3} T$	438–523	438
0.800	$C_p = 24.547 + 4.115 \times 10^{-3} T$	373–523	373

T_{equ} and x_{CdTe}, coordinates of the solid ↔ $\text{solid}_{(1)} + \text{solid}_{(2)}$ equilibria.

TABLE 4

Experimental and calculated values of the molar heat capacity of the CdTe–HgTe system at 500 K

x_{CdTe}	$C_{p(meas)}$	$C_{p(calc)}$	ΔC_p(excess)
0.000	27.48	27.48	0
0.0996	27.13	27.42	−0.29
0.118	27.48	27.40	+0.08
0.253	27.17	27.30	−0.13
0.350	26.57	27.23	−0.66
0.400	26.51	27.20	−0.69
0.500	26.21	27.13	−0.92
0.544	26.32	27.10	−0.78
0.600	26.34	27.06	−0.72
0.700	26.35	26.99	−0.64
0.800	26.60	26.92	−0.32
1	26.78	26.78	0

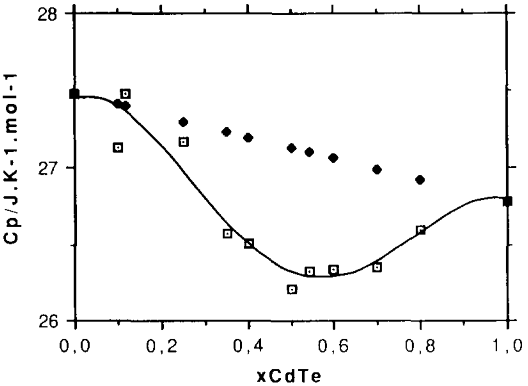

Fig. 5. Calculated (◆) and experimental (□) values of molar heat capacity of CdTe–HgTe alloy at 500 K *vs.* x_{CdTe}.

For each alloy, we deduced the $C_p=f(T)$ equation from C_p values obtained in the single-phase region (see Table 3). Using these relations, the values of excess molar heat capacity ($\Delta C_p = C_{p(exp)} - C_{p(calc)}$) were calculated at 500 K (see Table 4). In the single-phase region, all the ΔC_p values are negative for the entire range of composition ($\Delta C_p=f(x_{CdTe})$ curve, Fig. 5); the extremum value of the excess molar heat capacity is located at $x_{CdTe}=0.5$.

4. Conclusion

In some solid systems, a correlation has been observed between positive departure from Vegard's law and the occurrence of a miscibility gap inside the temperature–composition diagram. In this system no systematic trend or correlation appears between the zero-departure of Vegard's law and the structural features of the CdTe–HgTe solid solution.

The shape of $C_p = f(T)$ curves obtained between 300 K and 523 K suggests the existence of a miscibility gap in CdTe–HgTe solid alloys with a critical point at $x_{CdTe} = 0.55$ with $T = 455$ K. Moreover, in the single-phase solid region limited by the solidus curve and the miscibility gap, the excess molar heat capacity of CdTe–HgTe alloys is negative; this minimum of configurational entropy for the equiatomic solution probably corresponds to an ordering process in the lattice.

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