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# A thermodynamic evaluation of the Mn–Te binary system

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## Abstract

Because the MnTe compound is a promising material for semi-conductor applications when incorporated in multi-component alloys, the Mn–Te binary system has been critically assessed using an optimization procedure. An original set of self-consistent parameters has been established for the liquid phase, described with a non-ideal associate model, and for the non-stoichiometric compounds MnTe and $MnTe_2$, described with a multi-sublattice model. The phase diagram and characteristic thermodynamic properties have been calculated and compared with the experimental values. The uncertainty in the experimental phase diagram is discussed relative to the thermodynamic modelling. The thermodynamic modelling is consistent with a congruent melting of MnTe.

## INTRODUCTION

According to Johnston and Sestrich [1], the MnTe compound presents the "NiAs" hexagonal structure with the lattice parameters $a = 4.148$ Å and $c = 6.710$ Å ($\alpha$-phase) at low temperatures. Allen et al. [2] state that its semi-conductor properties correspond to a band width of $E_g \approx 1.3$ eV at room temperature. At 955°C (1228 K), the first transformation occurs, which leads to the $\beta$-phase (blende cubic structure), its lattice parameter being estimated as 6.34 Å by extrapolating one of the $Mn_{1-x}Cd_xTe$ pseudo-binary solid solutions published by Lee and Ramdas [3]. According to Gunshor et al. [4], the $\beta$-phase also has semi-conductor properties ($E_g \approx 3.2$ eV). Above 1020°C (1293 K), MnTe is again hexagonal (wurzite $\gamma$-phase, $a = 4.148$ Å and $c = 6.721$ Å [5]). A final transformation occurs at 1055°C (1328 K) to yield the $\delta$-phase with the NaCl cubic structure ($a = 6.026$ Å [1]).

The practical interest in MnTe lies in its capacity to form "blende"

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structure pseudo-binary solid solutions with $II_B$ (where $II_B$ is Cd, Hg, Zn) metal tellurides. Giebultowicz et al. [6] have determined that the paramagnetic cation $Mn^{2+}$ introduces low-temperature lattice spin glass properties when the Mn content is low, and antiferromagnetic properties at higher Mn concentrations.

These alloys have magneto-optical properties (Faraday rotation) that are intersting in electronics applications (preventing laser beam retro-diffusion in its own cavity, current censors, etc.)

From a strictly metallurgical point of view, the addition of Mn to the II–VI compounds allows the fabrication of electronical devices, among which are suitable substrates or plug coatings in infrared detectors replacing Cd–Te [7, 8]. A recent application described by Molva et al. [9] is the use of Mn–Te as a starting material in compact lasers visible in the orange-yellow and the blue.

The thermodynamic modelling of the Mn–Te binary system using the program of Lukas et al. [10] is presented here. The thermodynamic properties have been critically assessed with respect to the phase diagram, because they are needed for calculating and understanding processes of MnTe-based multi-component solid solutions.

## EXPERIMENTAL INFORMATION

### *Phase diagram*

The phase diagram of the Mn–Te system has been studied by different authors, not always in good agreement.

Thermal, microstructural and X-ray analyses, and micro-hardness measurements were used by Abrikosov et al. [11] to construct the phase diagram of the Mn–Te system. Two intermediate compounds, MnTe and $MnTe_2$, were identified. The maximum region of homogeneity of MnTe at 1050°C (1323 K) is 46.4–51 at.% Te, and that of $MnTe_2$ at 450°C (723 K) is 62.7–66.6 at.% Te. A polymorphic transformation between the hexagonal and cubic forms occurs in the range 990–1020°C (1263–1293 K). On the Mn-rich side, the pahse diagram shows a miscibility gap with a monotectic temperature of 1108°C (1381 K), and an eutectic reaction at 1056°C (1329 K). On the Te-rich side, $MnTe_2$ melts peritectally at 735°C (1008 K) and a degenerate eutectic occurs at 540°C (723 K). According to these authors, MnTe melts congruently at 1165°C (1438 K).

Using contactless thermography, X-ray analysis and DTA experiments, Vanyarko et al. [12] proposed a different version of the phase diagram on the Mn-rich side. The monotectic temperature (1230 ± 10°C, 1503 K) is higher than that determined by Abrikosov et al. [11], and the MnTe compound melts peritectically at (1155 ± 5°C, 1428 K). The phase transformations of MnTe have been represented by the scheme $\alpha \leftrightarrow \beta$ at 955°C (1228 K); $\beta \leftrightarrow \gamma$ at 1020°C (1293 K); $\gamma \leftrightarrow \delta$ at 1055°C (1328 K). The $\alpha$- and $\delta$-forms are manganese tellurides of the NiAs and NaCl structural types, respectively, while the $\beta$- and $\gamma$-forms correspond to modifications of the sphalerite and wurzite structural types, respectively.

Thermal effects have been observed at 745°C (1018 K), 1085°C (1358 K) and 1180°C (1453 K) and are associated with the Mn transformations. These differ from those accepted by the SGTE (Scientific Group Thermodata Europe), which are respectively 707°C (980 K), 1087°C (1360 K) and 1138°C (1411 K) [13].

The Te-rich side of the diagram has been carefully determined by Mateika [14] using DTA analysis, with an accuracy of ±3 K. It presents a congruent melting point for MnTe (1165 ± 3°C, 1438 K), and a peritectic reaction on the Te-rich side at 730 ± 10°C (1003 K). The transformation between the hexagonal and cubic forms was found to be at 1026 ± 3°C (1299 K).

A phase diagram combining the experimental results of Abrikosov et al. [11] on the Mn-rich side and Mateika [14] on the Te-rich side has been plotted by Pajaczkowska [15].

Using thermal analysis and crystallographic studies, Kasai and Nishihara [16] have located the peritectic reaction on the Te-rich side at 724 ± 2°C (1015 K).

The composition and temperature of all the invariant reactions reported by different authors are given in Table 2 and are discussed below, where they are compared with values calculated in the present work.

## *Crystallography*

The MnTe compound has the NiAs-type ($B_8$) hexagonal structure at low temperatues ($\alpha$-phase), with the following published lattice parameters: $a = 4.132$ Å, $c = 6.712$ Å, $c/a = 1.624$ (Oftedal [17]); $a = 4.146$ Å, $c = 6.709$ Å, $c/a = 1.618$ (Furberg [18]); $a = 4.087 \pm 0.001$ Å, $c = 6.701 \pm 0.002$ Å, $c/a = 1.640$ (Grazhdankina and Gurfel [19]); $a = 4.143 \pm 0.002$ Å, $c = 6.711 \pm 0.003$ Å, $c/a = 1.620$, (Makovetskii and Sirota [20]); $a = 4.148$ Å, $c = 6.710$ Å, $c/a = 1.618$ (Johnston and Sestrich [21]); $a = 4.155 \pm 0.005$ Å, $c = 6.711 \pm 0.005$ Å, $c/a = 1.615$ (Vanyarko et al. [12]).

At 955°C (1228 K), the $\beta$-phase (cubic "blende"-type structure) has a lattice parameter of $a = 6.34$ Å, determined by extrapolating the value for $Mn_{1-x}Cd_xTe$ pseudo-binary solid solutions [3]. Above 1020°C (1293 K), MnTe is again hexagonal ($\gamma$-phase, wurzite type), with $a = 4.148$ Å and $c = 6.721$ Å (Griffiths [5]). At high temperatures, above 1055°C (1328 K),

$\delta$-MnTe is face-centred cubic, NaCl type, with a published lattice parameter $a = 6.026 \pm 0.004$ Å (Johnston and Sestrich [1]) and $a = 5.98$ Å (Griffiths [5]).

$MnTe_2$ has the $FeS_2$ ($C_2$) type structure with the published lattice parameter $a = 6.957$ Å (Oftedal [22] and Elliott [23]) and $a = 6.951$ Å (Furberg [18]).

## *Thermodynamic properties*

### *Liquid*

Using dissolution calorimetry, Maekawa and Yokokawa [24] have measured the partial molar excess enthalpy of solid Mn in liquid Te at infinite dilution as $\delta\bar{H}^{\infty}_{\mathrm{Mn}} = -44099 \pm 3766\ \mathrm{J\ mol^{-1}}$ and at 741 K. The enthalpy of formation in the homogeneous liquid phase is linear up to the solubility limit $x_{\mathrm{Mn}} = 0.0018$. Other experimental measurements would be needed for a better knowledge of the enthalpy of mixing versus temperature and composition.

### *MnTe*

The heat capacity as reported by Barin and Knacke [25], and Barin [26] is the one given by Mills [27] in the temperature range 307–1438 K. Data in the temperature range 54–327 K come from Kelley [28] and give the heat content $[H^{\ominus}(298.15\ \mathrm{K}) - H^{\ominus}(0\ \mathrm{K})] = 6994\ \mathrm{J\ mol^{-1}}$. A $\lambda$-type transition was observed at 327 K, with a decrease in the heat capacity from a maximal value of 38.451 to 28.765 $\mathrm{J\ mol^{-1}}$

for $54 < T < 307$ K

$$C_p(\mathrm{Mn_{0.5}Te_{0.5}})/(\mathrm{J\ mol^{-1}}) = -40.794 + 257.65909 \times 10^{-3}T \tag{1a}$$

for $54 < T < 307$ K

$$C_p(\mathrm{Mn_{0.5}Te_{0.5}})/(\mathrm{J\ mol^{-1}}) = +28.3466 + 1.38072 \times 10^{-3}T \tag{1b}$$

Equation (1a) gives $C_p(298.15\ \mathrm{K}) = 36.027\ \mathrm{J\ mol^{-1}}$, which yields $\delta C_p(298.15\ \mathrm{K}) = 10.044\ \mathrm{J\ mol^{-1}}$, using the values from Hultgren et al. [29], $C_p(298.15\ \mathrm{K, Mn}) = 26.276\ \mathrm{J\ mol^{-1}}$ and $C_p(298.15\ \mathrm{K, Te}) = 25.690\ \mathrm{J\ mol^{-1}}$. From Kunitomi et al. [30], the transformation at 307 K is probably due to the oxidation of MnTe in MnO + $MnTe_2$.

The enthalpy of formation $\delta H^{\ominus}(298.15\ \mathrm{K}) = -54810 \pm 4180\ \mathrm{J\ mol^{-1}}$ reported by Barin [26] comes from an evaluation of Wiedemeier and Sadeek [31] by Knudsen's method. the determination by combustion calorimetry made by Morozova and Stolyarova [32] yields $\delta H^{\ominus}(298.15\,\mathrm{K}) = -55647 \pm 2720\,\mathrm{J\,mol^{-1}}$. More recently, Lukashenko et al. [33] have measured the Gibbs energy of formation of the compound in the temperature range 723–823 K by the electromotive force method and give $\delta G^{\ominus}(723\text{–}823\,\mathrm{K}) = -53555.2 - 9.12112T\ (\pm 418)\,\mathrm{J\,mol^{-1}}$.

The entropy $S(298.15\,\mathrm{K})$ is equal to $46.8608 \pm 0.8368\,\mathrm{J\,mol^{-1}\,K^{-1}}$ from Kelley [28]; this value was also reported by Mills [27], Barin and Knacke [25] and Barin [26]. The value of the entropy of formation from the pure elements is $\delta S^{\ominus}(298.15\,\mathrm{K}) = (46.8608 - 16.1103 - 24.74835) = +6.00215 \pm 0.8368\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

Very recently, Vassiliev et al. [34] have re-investigated the thermodynamic properties of the intermetallic compounds in the Mn–Te system by potentiometry and differential scanning calorimetry. Three equations were used to describe the heat capacity versus temperature, taking into account the measurements of Kelley [28] and their own measurements. The third is for $315 < T < 670\,\mathrm{K}$

$$C_p(\mathrm{Mn_{0.5}Te_{0.5}})/(\mathrm{J\,mol^{-1}}) = 39.363 - 4.675 \times 10^{-2}T + 5.523 \times 10^{-5}T^2 - 1.652 \times 10^{-8}T^3 \qquad (2)$$

From calorimetric and potentiometric experiments [34], the molar enthalpy, free energy and entropy were determined at 298.15 K:

$\delta H^{\ominus}(298.15\,\mathrm{K}) = -53300 \pm 800\,\mathrm{J\,mol^{-1}}$,

$\delta S^{\ominus}(298.15\,\mathrm{K}) = 8.0 \pm 1.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$,

$\delta G^{\ominus}(298.15\,\mathrm{K}) = -55600 \pm 200\,\mathrm{J\,mol^{-1}}$.

### *$MnTe_2$*

The heat capacity has been reported by Mills [27], Barin and Knacke [25] and Barin [26] in the temperature range 298.15–700 K, from an extrapolation of the heat capacity measurements of Westrum and Grønvold [35] in the range 5–350 K

$$C_p(\mathrm{Mn_{0.333}Te_{0.667}})/(\mathrm{J\,mol^{-1}}) = 25.550293 + 1.3946667 \times 10^{-3}T \qquad (3)$$

The heat capacity has been also determined by Wiedemeier and Sadeek [31] in the range 328–573 K

$$C_p(\mathrm{Mn_{0.333}Te_{0.667}})/(\mathrm{J\,mol^{-1}}) = 24.866907 + 1.71544 \times 10^{-3}T \qquad (4)$$

Equations (3) and (4) give respectively $C_p(298.15\,\mathrm{K}) = 25.966$ [5–27] and

25.378 J mol$^{-1}$ [30], corresponding respectively to $\delta C_p$(298.15 K) = +0.081 and −0.507 J mol$^{-1}$.

The recent work of Vassiliev et al. [34] using potentiometric and differential scanning calorimetry gives the heat capacity in the temperature range 298–723 K as

$$C_p(\mathrm{Mn_{0.333}Te_{0.667}})/(\mathrm{J\ mol^{-1}}) = 12.75 \pm 0.63 + (2.49 \pm 0.09) \times 10^{-2}T \qquad (5)$$

The enthalpy of formation $\delta H^{\ominus}$(298.15 K) has been estimated as −41840 ± 13947 J mol$^{-1}$ by Mills [27]. This value is also reported by Barin [26]. The experimental determination using Knudsen's method by Wiedemeier and Sadeek [36] yields $\delta H^{\ominus}$(298.15 K) = −36819.2 ± 2789 J mol$^{-1}$. The Gibbs energy of formation measured using an electromotive force method by Lukashenko et al. [33] in the temperature range 723–823 K is equal to $\delta G^{\ominus}$(723–823 K) = −40264.03 − 5.5368267$T$ (±209) J mol$^{-1}$.

The entropy $S^{\ominus}$(298.15 K) is given as 48.339147 J mol$^{-1}$ K$^{-1}$ by Westrum and Grønvold [35]; this is also the value reported by Mills [27], Barin and Knacke [25], and Barin [26]. The value of the entropy of formation from the pure elements is equal to $\delta S^{\ominus}$(298.15 K) = (48.339147 − 10.7402 − 32.9978) = +4.601147 J mol$^{-1}$ K$^{-1}$.

From the very recent results of Vassiliev et al. [34] obtained using a calorimetric and potentiometric method, the molar enthalpy, free energy and entropy were determined at 298.15 K as $\delta H^{\ominus}$(298.15 K) = −41800 ± 600 J mol$^{-1}$, $\delta S^{\ominus}$(298.15 K) = 2.6 ± 1.7 J mol$^{-1}$K$^{-1}$, $\delta G^{\ominus}$(298.15 K) = −42500 ± 200 J mol$^{-1}$. These authors claim that the homogeneity range of the Te-rich intermetallic compound is very narrow, namely $\mathrm{MnTe_{2.03\pm0.01}}$.

## THERMODYNAMIC MODELLING

The complete experimental data set containing both the phase diagram and the thermodynamic properties has been analysed.

Some primary discrimination was needed owing to the large discrepancies in the phase diagram determinations. On the Te-rich side, a maximal difference of about 90°C for the liquidus temperatures has been observed between the measurements of Abrikosov et al. [11] and Mateika [14]. This last author gives an accuracy of 3 K for the experimental values and the melting point of MnTe, and 10 K for the peritectic reaction. For these reasons, the experimental values of Mateika [14] have been considered more reliable on the Te-rich side than those of Abrikosov et al. [11].

Moreover, the liquidus shape shown in the diagram of Mateika [14] assumes a strong tendency to MnTe-associate formation in the liquid phase, due to the steep slope of the liquidus near the melting point of MnTe. The degenerate eutectic on the Te-rich side [11, 13, 14] and the miscibility gap described on the Mn-rich side by Abrikosov et al. [11] and Vanyarko et al. attests to a fairly different thermodynamic behaviour of the liquid phase in the two extreme parts of the diagram. Thus, the liquid phase was described using a non-ideal associate model (see Sommer [37]) as a mixture of free Mn and Te species, and MnTe associates, with the formula $(\mathrm{Mn, MnTe, Te})_1$. The interaction terms of the excess Gibbs energy were developed with a Redlich–Kister [38] polynomial.

The Gibbs energy of the liquid phase is given by the expression

$$G = G^{\text{Reference}} + G^{\text{Ideal}} + G^{\text{Excess}} \tag{6}$$

with

$$G^{\text{Reference}} = y_{\text{Mn}} G^{\ominus}_{\text{Mn}} + y\text{Te} G^{\ominus}_{\text{Te}} + y_{\text{MnTe}} G^{\ominus}_{\text{MnTe}} \tag{7}$$

$$G^{\text{Ideal}} = RT(y_{\text{Mn}} \ln y_{\text{Mn}} + y_{\text{Te}} \ln y_{\text{Te}} + y_{\text{MnTe}} \ln y_{\text{MnTe}}) \tag{8}$$

$$G^{\text{Excess}} = y_{\text{Mn}} y_{\text{Te}} L(\text{Mn,Te}) + y_{\text{Mn}} y_{\text{MnTe}} L(\text{Mn,MnTe}) + y_{\text{MnTe}} y_{\text{Te}} L(\text{MnTe, Te}) \tag{9}$$

In these equations, $G^{\ominus}_{\text{Mn}}$, $G^{\ominus}_{\text{Te}}$ and $G^{\ominus}_{\text{MnTe}}$ are the standard Gibbs energy of the pure liquid components Mn and Te [13] and of the associate MnTe, $Y_{\text{Mn}}$, $y_{\text{Te}}$ and $y_{\text{MnTe}}$ are the atomic fractions of Mn, Te or MnTe species, $L$ is the interaction term between these species and may vary with temperature and composition, $R = 8.31451\, J\, K^{-1}\, \text{mol}^{-1}$, and $T$ is the temperature in kelvin.

The experimental value $\delta \bar{H}^{\infty}_{\text{Mn}}$ of Maekawa and Yokokawa [24] imposes a constraint on the enthalpy of mixing of the liquid phase.

On the Mn-rich side, the accuracy of the experimental data is rather poor. Abrikosov et al. [11] present a eutectic reaction, while Vanyarko et al. propose a peritectic reaction [12]. As the very rapid evolution of the Te content of the liquid phase from about 0.39 to 1230°C (1503 K) to about 0.506 at 1155°C (1428 K) is not compatible with a simplified associate model, we have selected the phase diagram of Abrikosov et al. [11] on the Mn-rich side, with a eutectic reaction. However, the eutectic temperature (1056°C, 1329 K) and the monotectic temperature (1108°C or 1381 K) should be determined more accurately.

Because MnTe has a non-stoichiometric range below and above the strictly stoichiometric composition (0.5), this phase has been described using a two-sublattice model according to Hillert [39], with the following formula $(\text{Mn, Va1})_a(\text{Te, Va2})_c$, by assuming the presence of vacancies on both the Mn (Va1) and Te (Va2) lattices. The non-stoichiometric range of $\text{MnTe}_2$ is only on the left side (<0.667), and thus vacancies (Va2) have been considered only on the Te sublattice. The numbers of atomic sites on each sublattice are respectively $a = 1$, $c = 1$ for MnTe, and $a = 1$, $c = 2$ for $\text{MnTe}_2$.

An expression similar to eqn. (6) is used to describe the Gibbs energy of the compounds

$$G^{\text{Reference}} = y_{\text{Mn}}\, y_{\text{Te}}\, G^{\ominus(\text{C})}_{\text{Mn}_a\text{Te}_c} + y_{\text{Mn}}\, y_{\text{Va2}}\, G^{\ominus(\text{C})}_{\text{Mn}_a\text{Va2}_c} + y_{\text{Va1}}\, y_{\text{Te}}\, G^{\ominus(\text{C})}_{\text{Va1}_a\text{Te}_c} + y_{\text{Va1}}\, y_{\text{Va2}}\, G^{\ominus(\text{C})}_{\text{Va1}_a\text{Va2}_c} \qquad (10)$$

$$G^{\text{Ideal}} = RTa(y_{\text{Mn}} \ln y_{\text{Mn}} + y_{\text{Va1}} \ln y_{\text{Va1}}) + RTc(y_{\text{Te}} \ln y_{\text{Te}} + y_{\text{Va2}} \ln y_{\text{Va2}}) \qquad (11)$$

$$G^{\text{Excess}} = y_{\text{Mn}}\, y_{\text{Va1}}\, L(\text{Mn, Va1}) + y_{\text{Te}}\, y_{\text{Va2}}\, L(\text{Te, Va2}) \qquad (12)$$

where $G^{\ominus(\text{C})}_{\text{Mn}_a\text{Te}_c}$, $G^{\ominus(\text{C})}_{\text{Mn}_a\text{Va2}_c}$, $G^{\ominus(\text{C})}_{\text{Va1}_a\text{Te}_c}$ and $G^{\ominus(\text{C})}_{\text{Va1}_a\text{Va2}_c}$ are the standard Gibbs energies of the pure reference components, having the structure of the compound (C) and obtained following a circular permutation by assuming that each sublattice is successively completely fulfilled by one constituent. Thus, $\text{Mn}_a\text{Te}_c$ corresponds to the pure stoichiometric compound, and $\text{Mn}_a$ $\text{Va2}_c$ and $\text{Va1}_a\text{Te}_c$ to the pure elements Mn and Te having the structure of the compound (C), i.e. hexagonal for MnTe at low temperatures and $\text{FeS}_2$-type for $\text{MnTe}_2$. The entity $\text{Va1}_a\text{Va2}_c$ has no physical meaning and its Gibbs energy has been assumed to be zero. The $y$ quantities are the atomic fraction of the constituents on ech sublattice, $L$ is the interaction term between these constituents on each sublattice and may vary with temperature and composition, $R = 8.31451\ \text{J K}^{-1}\ \text{mol}^{-1}$, and $T$ is the temperature in kelvin.

## OPTIMIZATION RESULTS

The values of the Gibbs energy of transformation between the different possible structures, or "lattice-stabilities", of the pure elements, Mn and Te, are taken from the SGTE database [13].

The coefficients of the Gibbs energy of formation of the MnTe associate, and of the excess Gibbs energy of the liquid phase, L(Mn, MnTe), L(MnTe, Te) and L(Mn, Te), those of the Gibbs energy of formation of the stoichiometric compounds MnTe and $\text{MnTe}_2$ referred to the pure components, and of the excess Gibbs energy of the non-stoichiometric compounds, L(Mn, Va1) and L(Te, Va2), have been optimized in consistency with the selected experimental information after a primary discrimination using the program of Lukas et al. [10]. All data are given in the Table 1.

## COMPARISON WITH THE EXPERIMENTAL INFORMATION

### *Phase diagram*

The phase diagram has been calculated using the optimized coefficients and is compared graphically with the experimental measurements of the different authors in Fig. 1.

TABLE 1

Optimized Gibbs energy coefficients of the different phases in the Mn–Te binary system in J $\mathrm{mol}^{-1}$

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Liquid

$G^{(L)}_{\mathrm{MnTe}} - G^{\ominus(L)}_{\mathrm{Mn}} - G^{\ominus(L)}_{\mathrm{Te}} = -119986.54 + 6.64533T$

$L(\mathrm{Mn,Te}) = 0.00$

$L(\mathrm{Mn,MnTe}) = 21096.04 + 8259.15(y_{\mathrm{Mn}} - y_{\mathrm{MnTe}})$

$L(\mathrm{MnTe,Te}) = 26979.32 - 21.15210T$

MnTe

$G(\mathrm{Mn_{0.5}Te_{0.5}}) - 0.5G^{\ominus(\mathrm{MnTe})}_{\mathrm{Mn}} - 0.5G^{\ominus(\mathrm{MnTe})}_{\mathrm{Te}} = -59515.12 - 7.44012T$

$G^{\ominus(\mathrm{MnTe})}_{\mathrm{Mn}} - G^{\ominus(\mathrm{bccA12})}_{\mathrm{Mn}} = 10000$

$G^{\ominus(\mathrm{MnTe})}_{\mathrm{Te}} - G^{\ominus(\mathrm{hex})}_{\mathrm{Te}} = 2000$

$L(\mathrm{Mn, Va1}) = +40218.03 - 29.33765T$

$L(\mathrm{Te, Va2}) = +13724.02$

$\mathrm{MnTe_2}$

$G(\mathrm{Mn_{0.333}Te_{0.667}}) - 0.333G^{\ominus(\mathrm{MnTe_2})}_{\mathrm{Mn}} - 0.667G^{\ominus(\mathrm{MnTe_2})}_{\mathrm{Te}} = -40830.51 - 3.56340T$

$G^{\ominus(\mathrm{MnTe_2})}_{\mathrm{Mn}} - G^{\ominus(\mathrm{bccA12})}_{\mathrm{Mn}} = 2000$

$L(\mathrm{Te, Va2}) = -128879.50 + 67.52942T$

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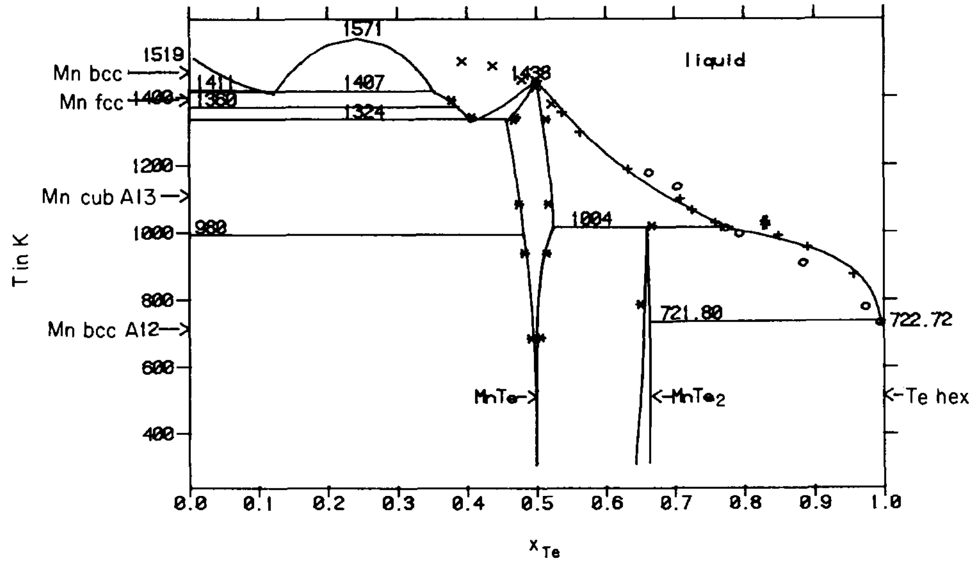

Fig. 1. Comparison between the calculated (present work) and experimental (literature) phase diagram of the Mn–Te system. O, Abrikosov et al. [11]; ×, Vanyarko et al. [12]; +, Mateika [14]; *, Pajaczkowska [15]; #, Kasai and Nishihara [16].

TABLE 2

Invariant equilibria and congruent transformations in the Mn–Te system

| Transformation | Experimental | | Calculated | | Ref. |
|---|---|---|---|---|---|
| | $T$/K | $x = x_{\mathrm{Te}}^{(\mathrm{L})}$ | $T$/K | $x = x_{\mathrm{Te}}^{(\mathrm{L})}$ | |
| Mn bccA12 ↔ Mn cubA13 | 980 | 0.000 | 980 | 0.000 | 13 |
| Mn cubA13 ↔ Mn fccA1 | 1360 | 0.000 | 1360 | 0.000 | 13 |
| Mn fccA1 ↔ Mn bccA2 | 1411 | 0.000 | 1411 | 0.000 | 13 |
| Mn bccA2 ↔ Mn liq | 1519 | 0.000 | 1519 | 0.000 | 13 |
| Te tri ↔ Te liq | 722.72 | 1.000 | 722.72 | 1.000 | 13 |
| (L) ↔ Mn $\mathrm{Te_2}$ + Te hex | 723 | 0.99 | 721.80 | 0.996 | 11, 14 |
| (L) + MnTe ↔ Mn $\mathrm{Te_2}$ | 1008 | 0.79 | 1003.80 | 0.782 | 11 |
| | 1003 ± 10 | 0.77 | | | 14 |
| | 1015 ± 2 | 0.83 | | | 16 |
| (L) ↔ MnTe | 1438 ± 3 | 0.50 | 1438.50 | 0.499 | 11, 14 |
| (L) + Mn bccA2 ↔ MnTe | 1428 | 0.506 | Not calculated | | 12 |
| (L1) ↔ Mn bccA2 + (L2) | 1503 | 0.010<br>0.390 | Not calculated | | 12 |
| (L2) ↔ Mn cubA13 + MnTe | 1329 | 0.41<br>0.464 | 1324.30 | 0.406<br>0.458 | 11 |
| (L1) ↔ Mn fcc + (L2) | 1381 | 0.37 | 1406.70 | 0.354<br>0.122 | 11 |
| (L1) ↔ (L2) | Not observed | | 1571 | 0.24 | |

The calculated invariant equilibria and the congruent transformations in the Mn–Te system are compared numerically to the experimental ones in Table 2.

## *Thermodynamic properties*

### *Liquid*

The partial molar excess enthalpy at infinite dilution of solid manganese in liquid tellurium at 741 K is equal to

$$\begin{aligned}\delta \bar{H}_{\mathrm{Mn}}^{\infty} &= L(\mathrm{MnTe}, \mathrm{Te}) + [H_{\mathrm{MnTe}}^{(\mathrm{L})} - H_{\mathrm{Mn}}^{(\mathrm{L})} - H_{\mathrm{Te}}^{(\mathrm{L})}] + [H_{\mathrm{Mn}}^{(\mathrm{L})} - H_{\mathrm{Mn}}^{(\mathrm{S})}] \\ &= 26979 - 112810 + 17863 = -67968\ \mathrm{J\ mol^{-1}}\end{aligned}$$

This value should be compared with the experimental value of Maekawa and Yokokawa [24], −44099 ± 3766 J $\mathrm{mol^{-1}}$.

### *$Mn_{0.5}Te_{0.5}$*

The calculated enthalpy and entropy of formation at room temperature are respectively $\delta H^{\ominus}(\mathrm{Mn_{0.5}Te_{0.5}}, 298.1\ \mathrm{K}) = -53515\ \mathrm{J\ mol^{-1}}$ and $\delta S^{\ominus}(\mathrm{Mn_{0.5}Te_{0.5}}, 298.15\ \mathrm{K}) = +7.544\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

The calculated enthalpy of formation at 298.15 K is greater by

2132 J $mol^{-1}$ than the experimental value of Morozova and Stolyarova [32] ($-55647 \pm 2720$ J $mol^{-1}$), by 1295 J $mol^{-1}$ than the value of Wiedemeier and Sadeek [31] ($-54810 \pm 4180$ J $mol^{-1}$), by 40 J $mol^{-1}$ than the value of Lukashenko et al. [33] ($-53555.2 \pm 418$ J $mol^{-1}$; $T = 723$–$823$ K)), and lower by 215 J $mol^{-1}$ than the value of Vassiliev et al. [34] ($-53300 \pm 800$ J $mol^{-1}$).

The calculated entropy of formation at 298.15 K is lower by 1.58 J $mol^{-1}$ $K^{-1}$ than the experimental value of Lukashenko et al. [33] (9.121 J $mol^{-1}$ $K^{-1}$), by 0.46 J $mol^{-1}$ $K^{-1}$ than the value of Vassiliev et al. [34] ($8 \pm 1.7$ J $mol^{-1}$ $K^{-1}$), and greater by 1.54 J $mol^{-1}$ $K^{-1}$ than the value of Kelley [28] ($6.00215 \pm 0.8368$ J $mol^{-1}$ $K^{-1}$).

### $Mn_{0.333}Te_{0.667}$

The calculated enthalpy and entropy of formation at room temperature are respectively $\delta H^{\ominus}(Mn_{0.333}Te_{0.667}, 298.15\ K) = -40164$ J $mol^{-1}$ and $\delta S^{\ominus}(Mn_{0.333}Te_{0.667}, 298.15\ K) = +3.564$ J $mol^{-1}$ $K^{-1}$.

The calculated enthalpy of formation at 298.15 K is greater by 1676 J $mol^{-1}$ than the experimental value of Mills [27] ($-41840 \pm 13947$ J $mol^{-1}$), by 1636 J $mol^{-1}$ than the value of Vassiliev et al. [34] ($-41800 \pm 600$ J $mol^{-1}$), lower by 3348 J $mol^{-1}$ than the value of Wiedemeier and Sadeek [36] ($-36819.2 \pm 2789$ J $mol^{-1}$) and by 100 J $mol^{-1}$ than the value of Lukashenko et al. [33] ($-40264 \pm 209$ J $mol^{-1}$; $T = 723$–$823$ K)).

The calculated entropy of formation at 298.15 K is lower by 1.97 J $mol^{-1}$ $K^{-1}$ than the experimental value of Lukashenko et al. [33] (5.537 J $mol^{-1}$ $K^{-1}$), by 1.04 J $mol^{-1}$ $K^{-1}$ than the value of Westrum and Gronvøld [35] (4.601 J $mol^{-1}$ $K^{-1}$) and greater by 0.96 J $mol^{-1}$ $K^{-1}$ than the value of Vassiliev et al. [34] ($2.6 \pm 1.7$ J $mol^{-1}$ $K^{-1}$).

## DISCUSSION

The agreement between the calculated experimental and the phase diagram is quite satisfactory. The diagram of Mateika [14] is well reproduced on the Te-rich side, with a congruent melting point calculated at 1438 K for MnTe. The thermodynamic modelling gives arguments in favour of a eutectic reaction on the Mn-rich side. However, further experimental information is necessary to improve the accuracy of the phase diagram in this domain. The non-stoichiometry range of MnTe is well represented. The structural transformations of MnTe have not been modelled due to the lack of thermodynamic information concerning the enthalpies of the transformations between the different possible structures.

The partial excess enthalpy of manganese in liquid tellurium at infinite dilution imposes a strongly positive interaction term, $L(MnTe, Te)$, and leads to a much less negative enthalpy of mixing of the liquid phase than if this experimental value whose accuracy is poor, is not taken into account. Thus, experimental values for the enthalpy of mixing of the liquid phase over a larger range of composition and temperature are recommended for further experimental studies.

According to the experimental uncertainties, the agreement between the calculated and experimental enthalpies and entropies of formation of both $Mn_{0.5}Te_{0.5}$ and $Mn_{0.333}Te_{0.667}$ is quite satisfactory. Due to the large discrepancies in the heat capacities reported by different authors, the difference $\delta C_p$ related to the pure solid components (Mn bccA12 and Te hex) has been neglected as a first approximation. If more accurate experimental values of $\delta C_p$ were available, they could be fixed in the optimization procedure.

## CONCLUSIONS

This thermodynamic evaluation of the Mn–Te system has allowed a self-consistent set of parameters for the liquid phase and the non-stoichiometric compounds MnTe and $MnTe_2$ to be produced. These new parameters can be used for calculating thermodynamic properties and phase diagram of the Mn–Te system, or of multi-component systems containing both these two elements. We also emphasize the necessity of further experimental studies, especially in the Mn-rich region of the phase diagram, and concerning the enthalpy of mixing of the liquid phase and the heat capacities of the compounds at high temperature.

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