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## A thermodynamic and structural analysis of selenium–tellurium melts

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**Abstract.** The thermodynamic properties of the selenium–tellurium system are analysed in terms of a novel regular solution model with multiple connectivity. The model is an extension of the regular solution model that discriminates between two forms of tellurium atom according to their connectivity (number of first neighbours). In the resulting ternary system, the chemical equilibrium between these two forms of tellurium is taken into account. The model can be solved in either the Bragg–Williams or the quasi-chemical approximation. A very good representation of the thermodynamic properties is obtained. Moreover, the model predicts a temperature and concentration evolution of the number of first neighbours in the liquid in close agreement with independent neutron scattering measurements. As a result, this model provides a simple insight into the mechanisms that are responsible for the complex thermodynamic and structural behaviour of the Se–Te system.

### 1. Introduction

The selenium–tellurium system has been extensively studied because of its complex behaviour regarding structural, thermodynamic and electrical properties. The two elements display close similarities: they have the same number of valence electrons (their p band is two-thirds filled with four electrons) and their stable crystalline phases are trigonal arrangements of helical chains. Their crystal structure derives from a Peierls distortion of a simple cubic structure, Se being more distorted than Te, as can be seen from the ratios of their shortest intrachain ( $r_s$ ) to interchain ( $r_l$ ) bonds lengths:  $r_s/r_l = 0.67$  for Se and 0.83 for Te. Although rather similar in the solid state, they differ in the liquid state. Elemental selenium is a semiconductor in both solid and liquid states at normal pressure and its liquid structure consists mainly of chains. It eventually undergoes a semiconductor-to-metal transition in the liquid state, in a region that lies in the vicinity of its critical point ( $P = 380$  bar,  $T = 1630$  °C) [1]. Tellurium becomes metallic upon melting [2], with a coordination number varying between 2.2 and 2.5 at the melting point and 3 at higher temperatures, according to various x-ray and neutron scattering experiments [3, 4, 5]. The metallic behaviour of liquid tellurium is now believed to be related to an enhancement of the interchain interactions as one of the interchain bonds is substantially shortened upon melting [6]. Liquid tellurium then appears as entangled broken chains, formed by a mixture of twofold- and threefold-coordinated atoms, whose relative proportions vary with temperature. In the case of selenium, the distance between the chains is comparatively larger, and consequently, the melt remains semiconducting over a broad temperature and pressure range. In molten Se–Te alloys the semiconductor–metal transition takes place at

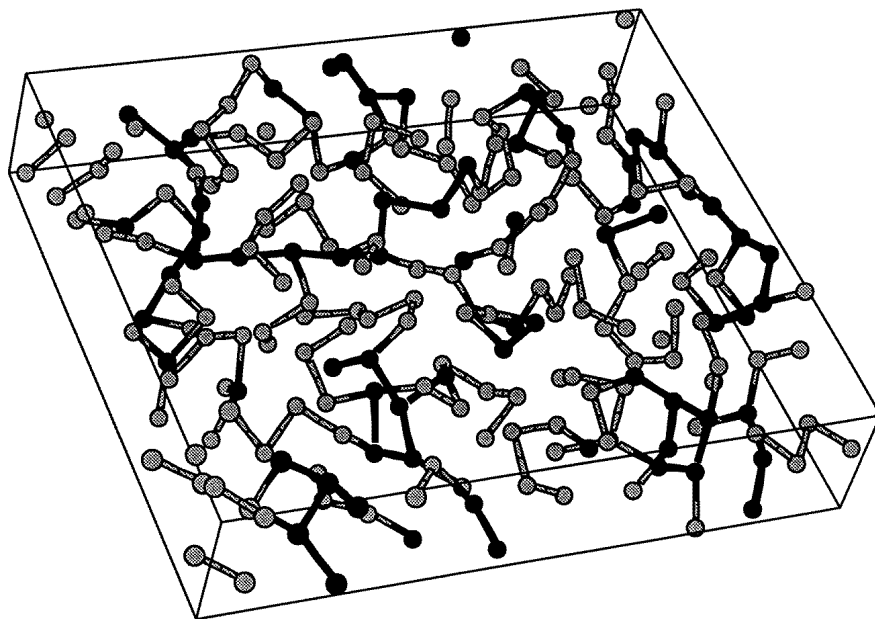
around 60–80% Te according to optical measurements (Raman scattering [7], reflectivity [8]). Neutron scattering experiments [9, 10] and EXAFS measurements [11] agree well with this scheme.

The structural changes in the melt are reflected in the thermodynamic quantities of mixing. As expected for such parent elements, the magnitude of the enthalpy and Gibbs energy of mixing is rather weak (of the order of some  $\text{kJ mol}^{-1}$ ) [12]. More interestingly, the enthalpy of mixing that is negative at low temperatures becomes positive in the Te-rich side with increasing temperature. Two different approaches to the thermodynamic modelling of the system have been followed. On the one hand a series of models (inhomogeneous structure model) assuming an inhomogeneous structure of the melt have been developed by Tsuchiya and Seymour [13]: a coexistence of metallic threefold-coordinated and semiconducting twofold-coordinated microdomains is assumed. This idea has been applied to explain various thermophysical properties of pure Te and Se–Te melts. It can be objected that microdomains containing approximately 10 to 30 atoms should give rise to small-angle features in the neutron scattering experiments, provided that the contrast between the domains is sufficient. Such features have not been observed to our knowledge. In [14] the thermodynamic properties of mixing of Se–Te have been derived. On the other hand, the thermodynamic quantities of mixing have been derived in terms of excess-volume contributions [15]. This approach assumes an ideal solution model for Se–Te and considers a series expansion of the  $P \Delta V$ -term to account for the excess term.

The aim of this paper is to analyse the close relationship between the atomic structure—characterized, in a first approximation, by the coordination number—and the thermodynamic quantities of mixing, with the help of a simple statistical model: the regular model with multiple connectivity (RMMC). The present model allows us to recast some of the basic assumptions of the inhomogeneous structural model in a clear framework and ultimately uses the thermodynamic properties of the binary system to probe the structure of one of the constitutive elements.

## 2. The regular solution model with multiple connectivity

The basic idea underlying this model is to consider that the changes of the thermodynamic properties of the molten Se–Te alloys are due to the structural changes undergone by tellurium as the temperature is raised. Such an idea has already been applied by Takeda *et al* [16] to analyse the temperature dependence of the structure factor of liquid Te obtained by neutron scattering. The main assumption is to treat the binary Se–Te system as a ternary one, by discriminating between two forms of tellurium atoms, according to their number of first neighbours (connectivity). The interpretation of the neutron or x-ray scattering experiments leading to the determination of the coordination numbers is not straightforward and has led to controversy. Even in the computer simulation results, the interpretation of the connectivity of pure liquid tellurium is not a simple matter. As explained in [6], the structure of liquid Te results from a significant shortening of one of the interchain bonds upon melting. The chain structure is preserved and the number of enhanced interchain bonds varies with temperature. For the purpose of thermodynamic modelling, it is reasonable to assume that selenium remains twofold coordinated and that tellurium atoms can be either twofold ( $\text{Te}^{\text{II}}$ ) or threefold ( $\text{Te}^{\text{III}}$ ) coordinated. This assumption is supported by the results of tight-binding Monte Carlo simulations performed by one of the authors [6]: figure 1 presents a snapshot of a configuration of liquid tellurium with  $\text{Te}^{\text{II}}$  and  $\text{Te}^{\text{III}}$  atoms distinguished by their colour. Beyond the different coordination numbers, it is interesting to notice a tendency towards phase separation between  $\text{Te}^{\text{II}}$  and  $\text{Te}^{\text{III}}$  atoms, which has been quantified in [6] by the



**Figure 1.** A typical configuration of liquid tellurium obtained by a tight-binding Monte Carlo simulation. A slab containing approximately 200 atoms has been cut out of the box of 1152 atoms. Atoms whose distance is less than  $3.15 \text{ \AA}$  are considered connected. Twofold-coordinated tellurium atoms are shown in grey, threefold-coordinated atoms are in black. Some atoms may appear less than twofold or threefold coordinated due to the periodic boundary conditions used. A tendency towards phase separation between  $\text{Te}^{\text{II}}$  and  $\text{Te}^{\text{III}}$  species appears and can be quantified by means of an order parameter. For details, see [6].

calculation of an order parameter. The general framework of our approach is the regular solution model and the present treatment closely follows that of Guggenheim [17], with two important differences:

- (i) the ‘quasi-lattice’ has no constant connectivity as the connectivity depends on the nature of the atoms; and
- (ii) the model explicitly describes the equilibrium  $\text{Te}^{\text{II}} \leftrightarrow \text{Te}^{\text{III}}$  in the presence of selenium.

Table 1 presents the notation used throughout this paper.

Pure tellurium is then considered as a ‘solution’ whose concentration ( $x$ ) in the  $\text{Te}^{\text{II}}$  species is

$$x = \frac{N'_2}{N'_2 + N'_3} = \frac{N_2}{N_2 + N_3} = \frac{N'_2}{N_{\text{Te}}}. \quad (1)$$

The total number of pairs in the solution is

$$P = \frac{z_1 N_1 + z_2 N_2 + z_3 N_3}{2}. \quad (2)$$

$P_{12}$  ( $P_{13}$ ,  $P_{23}$ ) denotes the number of Se– $\text{Te}^{\text{II}}$  (Se– $\text{Te}^{\text{III}}$ ,  $\text{Te}^{\text{II}}$ – $\text{Te}^{\text{III}}$ ) pairs. The energies of such pairs are  $\varepsilon_{12}$ ,  $\varepsilon_{13}$  and  $\varepsilon_{23}$  respectively. Under such assumptions, the total configurational

energy of the Se–Te solution is

$$\Phi = P_{12}(\varepsilon_{12} - \frac{1}{2}\varepsilon_{11} - \frac{1}{2}\varepsilon_{22}) + P_{13}(\varepsilon_{13} - \frac{1}{2}\varepsilon_{11} - \frac{1}{2}\varepsilon_{33}) + P_{23}(\varepsilon_{23} - \frac{1}{2}\varepsilon_{22} - \frac{1}{2}\varepsilon_{33}) + \frac{1}{2}z_1N_1\varepsilon_{11} + \frac{1}{2}z_2N_2\varepsilon_{22} + \frac{1}{2}z_3N_3\varepsilon_{33} \quad (3)$$

while that of pure Se is

$$\Phi_{\text{Se}} = \frac{1}{2}z_1N_1\varepsilon_{11} \quad (4)$$

and that of pure Te is

$$\Phi_{\text{Te}} = P'_{23}(\varepsilon_{23} - \frac{1}{2}\varepsilon_{22} - \frac{1}{2}\varepsilon_{33}) + \frac{1}{2}z_2N'_2\varepsilon_{22} + \frac{1}{2}z_3N'_3\varepsilon_{33} \quad (5)$$

where  $P'_{23}$  is the number of  $\text{Te}^{\text{II}}\text{--Te}^{\text{III}}$  pairs in pure tellurium.

**Table 1.** Notation.

Species	Number of atoms in the pure elements	Number of atoms in the alloy	Mole fraction in the alloy	Connectivity
Se	$N_1$	$N_1$	$X_1$	$z_1 = 2$
$\text{Te}^{\text{II}}$	$N'_2$	$N_2$	$X_2$	$z_2 = 2$
$\text{Te}^{\text{III}}$	$N'_3$	$N_3$	$X_3$	$z_3 = 3$

In a zeroth-order (Bragg–Williams) approximation, corresponding to a random distribution of the atomic species, the number of pairs of each kind is given by

$$P_{ij}^* = \frac{z_i z_j N_i N_j}{z_1 N_1 + z_2 N_2 + z_3 N_3} \quad (6)$$

and the configurational partition functions of the solution ( $\Omega$ ) and the pure elements ( $\Omega_{\text{Se}}$  and  $\Omega_{\text{Te}}$ ) can be easily calculated:

$$\Omega = \frac{(N_1 + N_2 + N_3)!}{N_1!N_2!N_3!} \exp - \frac{\phi(P_{12}^*, P_{13}^*, P_{23}^*)}{kT} \quad (7)$$

$$\Omega_{\text{Se}} = \exp - \frac{z_1 N_1 \varepsilon_{11}}{2kT} \quad (8)$$

$$\Omega_{\text{Te}} = \frac{(N_{\text{Te}})!}{N'_2!N'_3!} \exp - \frac{\phi_{\text{Te}}^*(P'_{23})}{kT}. \quad (9)$$

The combinatory term in (7) is obtained by a two-step procedure. We first calculate the number of ways to build a lattice with  $(N_1 + N_2)$  twofold- and  $N_3$  threefold-coordinated sites. We then count the number of atomic arrangements on such a lattice, allowing  $N_1$  Se and  $N_2$   $\text{Te}^{\text{II}}$  atoms to mix randomly on the  $(N_1 + N_2)$  twofold-coordinated sites. The combinatory term in (7) is the product of these two terms.

The Gibbs energy of mixing can be written quite generally as

$$\begin{aligned} \Delta G^m = & [X_3 - (1 - x)(1 - X_1)] \Delta G^0 + d \sum_{i \neq j} \left[ z_i z_j X_i X_j W_{ij} / \left( \sum_i z_i X_i \right) \right] \\ & + RT \sum_{i=1}^3 X_i \ln X_i \\ & - (1 - X_1) \left[ \frac{z_2 z_3 x (1 - x)}{z_2 x + z_3 (1 - x)} W_{23} + RT \{x \ln x + (1 - x) \ln(1 - x)\} \right] \quad (10) \end{aligned}$$

with  $W_{ij} = \mathcal{N}(\varepsilon_{ij} - \frac{1}{2}\varepsilon_{ii} - \frac{1}{2}\varepsilon_{jj})$ , where  $\mathcal{N}$  is Avogadro's number,  $\Delta G^0 = \Delta H^0 - T \Delta S^0$  and  $\Delta H^0 = \mathcal{N}((z_3/2)\varepsilon_{33} - (z_2/2)\varepsilon_{22})$ .  $\Delta G^0$  and  $\Delta S^0$  are the standard Gibbs energy and entropy of the transformation reaction  $\text{Te}^{\text{II}} \rightarrow \text{Te}^{\text{III}}$ .

In the particular case where  $z_1 = z_2 = 2$  and  $z_3 = 3$ ,  $\Delta G^m$  becomes

$$\begin{aligned} \Delta G^m = & [X_3 - (1-x)(1-X_1)] \Delta G^0 + \frac{2X_1X_2}{d} W_{12} + \frac{3X_1X_3}{d} W_{13} \\ & + \left[ \frac{3X_2X_3}{d} - (1-X_1) \frac{6x(1-x)}{3-x} \right] W_{23} + RT[X_1 \ln X_1 + X_2 \ln X_2 \\ & + X_3 \ln X_3 - (1-X_1)\{x \ln x + (1-x) \ln(1-x)\}] \end{aligned} \quad (11)$$

where  $d = X_1 + X_2 + \frac{3}{2}X_3$ .

The enthalpy of mixing  $\Delta H^m$  derives from  $\Delta G^m$ :

$$\begin{aligned} \Delta H^m = & [X_3 - (1-x)(1-X_1)] \Delta H^0 + \frac{2X_1X_2}{d} W_{12} + \frac{3X_1X_3}{d} W_{13} \\ & + \left[ \frac{3X_2X_3}{d} - (1-X_1) \frac{6x(1-x)}{3-x} \right] W_{23}. \end{aligned} \quad (12)$$

Until now the system has been treated as a regular ternary system—except for the variable connectivity. The second step is to express the equilibrium between  $\text{Te}^{\text{II}}$  and  $\text{Te}^{\text{III}}$  species: the equilibrium equation is obtained by minimizing the Gibbs energy of the solution Se–Te with respect to  $X_2$ . Remembering that pure tellurium is treated as a solution, we can write

$$G^m = \Delta G^m + X_1 G_{\text{Se}}^0 + (1-X_1) G_{\text{Te}}^m \quad (13)$$

with

$$G_{\text{Te}}^m = \Delta G_{\text{Te}}^m + x G_{\text{Te}^{\text{II}}}^0 + (1-x) G_{\text{Te}^{\text{III}}}^0$$

and

$$\Delta G_{\text{Te}}^m = \frac{6x(1-x)}{3-x} W_{23} + RT \{x \ln x + (1-x) \ln(1-x)\}.$$

One obtains

$$\begin{aligned} G^m = & X_1 G_{\text{Se}}^0 + X_2 G_{\text{Te}^{\text{II}}}^0 + X_3 G_{\text{Te}^{\text{III}}}^0 + \sum_{i \neq j} \left[ z_i z_j X_i X_j W_{ij} / \left( \sum_i z_i X_i \right) \right] \\ & + RT \sum_{i=1}^3 X_i \ln X_i. \end{aligned} \quad (14)$$

The equilibrium condition

$$\left. \frac{\partial G^m}{\partial X_2} \right|_{T,P} = 0$$

shows that  $X_2$  and  $X_3$  obey a mass action law:

$$\begin{aligned} RT \ln \frac{X_2}{X_3} = & \Delta G^0 - \frac{1}{d^2} [X_1(3-X_1)W_{12} \\ & + \frac{3}{2}\{(X_1+X_2)^2 - 4X_1 - 6X_2 + 3\}W_{23} - 3X_1W_{13}]. \end{aligned} \quad (15)$$

In the pure tellurium 'solution' ( $X_1 = 0 \rightarrow X_2 = x$  and  $X_3 = 1-x$ ), the above equation becomes

$$RT \ln \frac{x}{1-x} = \Delta G^0 - 6 \left( 1 - \frac{6}{(3-x)^2} \right) W_{23}. \quad (16)$$

In the high-temperature limit ( $T \rightarrow \infty$ ), this equation becomes

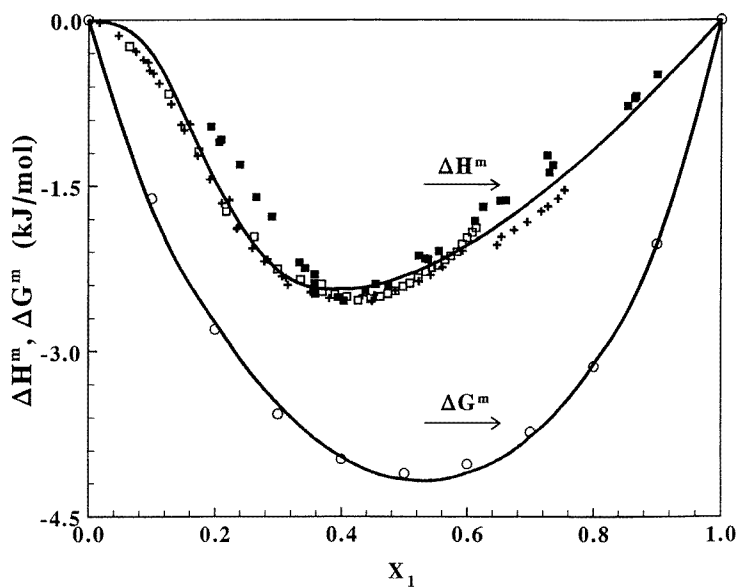
$$x = \frac{\exp(-\Delta S^0/R)}{[1 + \exp(-\Delta S^0/R)]}$$

### 3. Application to the Se–Te system

#### 3.1. Thermodynamic properties at 733 K

A large number of data on the enthalpy and Gibbs energy of mixing are available at 733 K [18, 19, 20]. Given  $n$  experimental values of  $\Delta H(X_1)$  and  $\Delta G(X_1)$  for  $n$  values of  $X_1$ , we are faced with a system of  $3n + 1$  equations ( $n$  equations (11), (12) and (15) respectively, and equation (16)) with  $n + 6$  unknowns, namely:  $W_{12}, W_{13}, W_{23}, \Delta H^0, \Delta G^0, x$ , and  $n$  values of  $X_2$ . The numerical resolution of this system proceeds in two steps:

- (i) calculate  $x$  and the  $n$  values of  $X_2$  using equations (15) and (16); and
- (ii) use an iterative least-squares fitting method to calculate the remaining adjustable parameters  $W_{12}, W_{13}, W_{23}, \Delta H^0, \Delta G^0$ , taking the equations (11), (12), (15), (16) into account.



**Figure 2.** The enthalpy of mixing and Gibbs free energy obtained by the RMMC at 733 K, in a Bragg–Williams approximation. The experimental data are obtained from the following: ■: [18]; +: [19]; □: [20]; ○: [20].

The effect of such an adjustment on the experimental data at 733 K is presented in figure 2. The agreement is very good, in particular on the Te-rich side, where the curvature of the enthalpy of mixing changes its sign, and where the minimum of  $\Delta H$  is observed. Such a behaviour is rather specific to the Se–Te system, and can hardly be reproduced by other thermodynamic models. The following set of adjustable parameters has been obtained

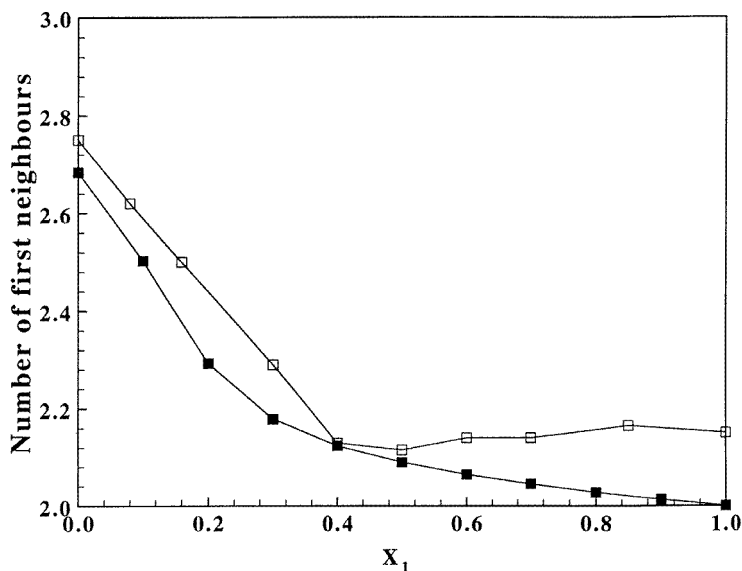
from the least-squares procedure described above:

$$\begin{aligned} W_{12} &= -0.871 \text{ kJ mol}^{-1} & W_{13} &= 3.489 \text{ kJ mol}^{-1} & W_{23} &= 4.370 \text{ kJ mol}^{-1} \\ \Delta H^0 &= 7.225 \text{ kJ mol}^{-1} & \Delta S^0 &= 10.299 \text{ J mol}^{-1} & x &= 0.316. \end{aligned}$$

The values of  $X_2$  obtained for each value of  $X_1$  are given in table 2. It can be seen that the addition of selenium favours the creation of  $\text{Te}^{\text{II}}$  species.

**Table 2.** Values of  $X_2$ .

$X_1$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$X_2$	0.39	0.51	0.52	0.47	0.41	0.34	0.26	0.17	0.08

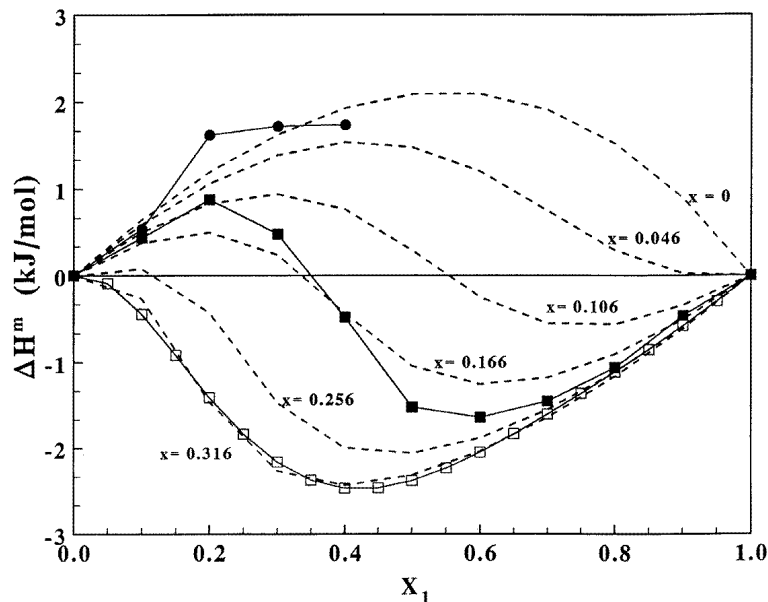


**Figure 3.** The number of first neighbours in liquid Se–Te alloys: ■: from RMMC simulation in a Bragg–Williams approximation; □: from neutron scattering experiments [9].

As expected, the magnitude of the  $W_{ij}$  is rather small. Their sign gives more insight into the physical behaviour of the Se–Te system. A weakly negative  $\text{SeTe}^{\text{II}}$  interaction is compatible with the existence of a continuous solid solution in the phase diagram. The interactions between species with different connectivity ( $\text{SeTe}^{\text{III}}$  and  $\text{Te}^{\text{II}}\text{Te}^{\text{III}}$ ) appear to be positive, indicating a tendency towards phase separation. Although these parameters are effective quantities whose physical interpretation requires some care, a positive value for  $W_{23}$  is in agreement with the results of the computer simulations quoted in [6]: the latter results show a clear tendency towards phase separation (see figure 1) that can be quantified by means of an order parameter. Of course, in the Bragg–Williams approximation used here this order parameter is zero. The model also yields structural information on the liquid. The value of  $x$  allows us to calculate an average coordination number for tellurium:

$$Z_{av}^{\text{Te}} = z_2x + z_3(1 - x) = 3 - x = 2.68 \quad (17)$$





**Figure 4.** The evolution of the enthalpy of mixing with  $x$  (the concentration of  $\text{Te}^{\text{II}}$  species in the pure tellurium ‘solution’). Increasing values of  $x$  correspond to increasing temperatures. The experimental values of the enthalpy of mixing were directly measured at 733 K (□) and calculated at 873 K (■) and 1073 K (●) (see the text).

which that is in good agreement with the experimental values.  $\Delta S^0 = 10.299 \text{ J mol}^{-1}$  yields a limiting high-temperature value of  $x = 0.22$ . This corresponds to a coordination number  $Z = 2.78$  for pure tellurium—a reasonable value, in view of the experimental uncertainties in the coordination number. More interestingly, the average coordination number over the whole concentration range of the Se–Te solution can be calculated from

$$Z_{av} = z_1 X_1 + z_2 X_2 + z_3 X_3 = 2X_1 + 2X_2 + 3X_3 \quad (18)$$

and compared to the results of neutron scattering experiments [9], as shown in figure 3. It has to be recalled that the values  $X_1, X_2, X_3$  have been obtained by fitting the thermodynamic data (the enthalpy and Gibbs energy of mixing). The successful comparison with structural data that have been measured independently is an indication of the validity of the model presented here.

### 3.2. Temperature effects

Another interesting point is to study the temperature dependence of the thermodynamic properties, remembering that a characteristic feature of the Se–Te system is the change of the sign of the enthalpy of mixing on the Te-rich side with increasing temperature. A complete fit of the thermodynamic data at different temperatures is hindered by the lack of reliable direct measurements of the enthalpy and Gibbs energy of mixing. Simply changing the temperature and retaining the values of  $W_{12}, W_{13}, W_{23}, \Delta H^0, \Delta G^0$  obtained by fitting at 733 K gives poor results. The temperature dependence of  $x$ , obtained by means of the equilibrium equation (17), is too weak to account for the changes in the thermodynamic quantities of mixing. This is partly due to the Bragg–Williams treatment

of the model that assumes a random distribution of the atomic species, for a system with a tendency towards ordering at low temperature and phase separation at high temperature. It is, however, possible to analyse the effect of the temperature indirectly by changing the value of  $x$  between 0.316 (its value at 733 K) and 0 (a value corresponding to very-high-temperature tellurium with only  $\text{Te}^{\text{III}}$  atoms), without changing the other parameters ( $W_{12}$ ,  $W_{13}$ ,  $W_{23}$ ,  $\Delta H^0$ ,  $\Delta G^0$ ). The enthalpy of mixing calculated for different values of  $x$  is shown in figure 4. The experimental values have been calculated from the data at 733 K and specific heat measurements from [21, 22, 23]. Although no quantitative agreement is obtained, the tendency of the sign of the enthalpy of mixing to change with increasing temperature is clearly present.

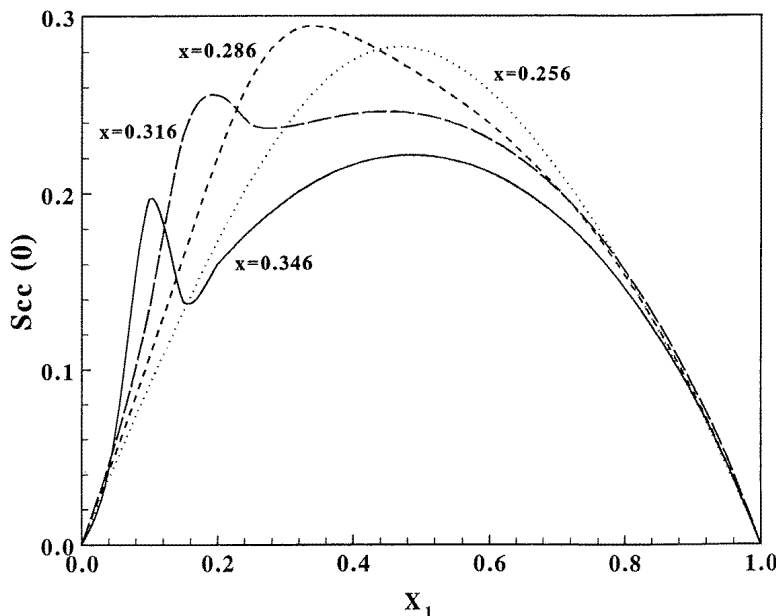
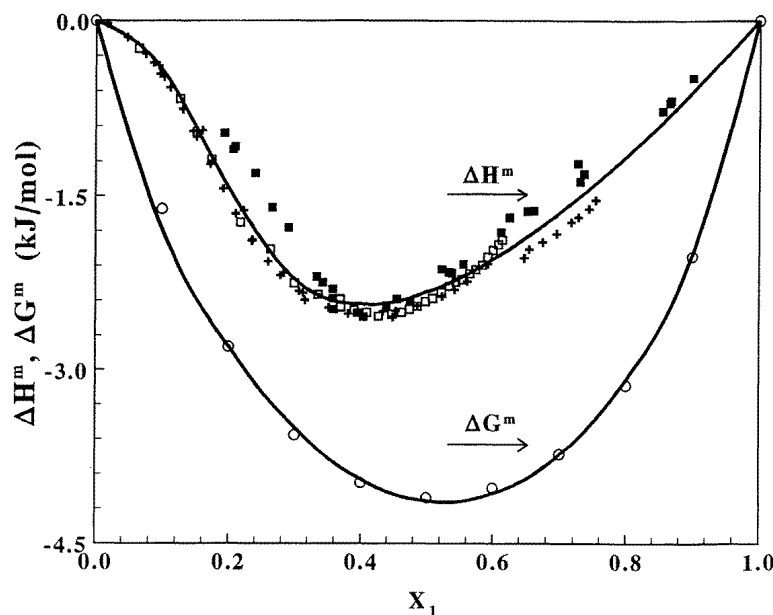


Figure 5.  $S_{cc}(0)$  as a function of the concentration of Se ( $X_1$ ) for different values of  $x$ .

The thermodynamic stability of the melt is related to the low-scattering-vector limit ( $q \rightarrow 0$ ) of the partial concentration–concentration structure factor  $S_{cc}(0)$  defined by Bhatia and Thornton [24]:

$$S_{cc}(0) = RT \left/ \left( \frac{\partial^2 G^m}{\partial X_1^2} \right)_{T,P,N} \right. \quad (19)$$

This quantity is plotted in figure 5 for different values of  $x$ . As the Gibbs energy depends directly on the temperature for the entropy term and indirectly for the enthalpy term, the significant range of  $x$  is narrower than that described above.  $S_{cc}(0)$  is always positive indicating that the solution is always stable, but the hump around  $X_1 = 0.2$  at 733 K, corresponding to  $x = 0.316$ , indicates a tendency towards phase separation. At higher temperature the positive value of the enthalpy of mixing is counterbalanced by the entropy term, so the hump disappears. Consequently, a peculiar behaviour of the low- $q$  structure factor, if present, should be better observed around the melting temperature and on the Te-rich side.

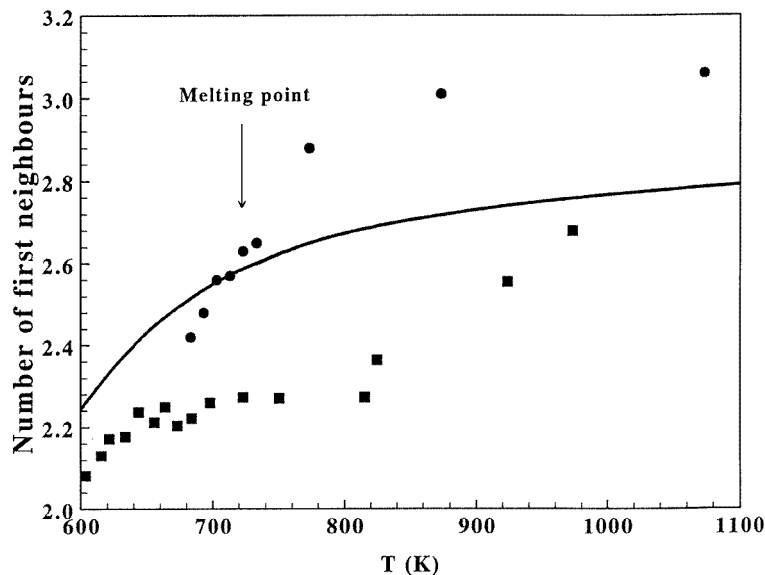


**Figure 6.** The enthalpy of mixing and Gibbs free energy obtained by RMMC simulation at 733 K, in a quasi-chemical approximation. The experimental data are obtained from the following work: ■: [18]; +: [19]; □: [20]; ○: [20].

The above calculations rely on a Bragg–Williams approximation. The ordering or phase separation effects can be better approximated in a quasi-chemical (QC) treatment. The resulting equations are given in appendix A. The values of the parameters obtained by fitting at 733 K differ only weakly from those of the Bragg–Williams treatment and a slight improvement of the agreement with the experimental data is observed on the tellurium-rich side of the system, as shown in figure 6. The evolution of the number of first neighbours in pure tellurium ( $Z_{av}^{Te}$ ) with temperature can be calculated from equation (17) with the value of  $x$  obtained by (23). It is plotted in figure 7, together with the experimental values taken from [25, 26]. Considering the experimental errors in the number of first neighbours, which are particularly awkward to obtain from neutron scattering data in the case of tellurium, the agreement is correct. It is observed that the number of first neighbours does not reach 3 in the temperature range of interest, indicating that a pure  $Te^{III}$  liquid is not obtained.

#### 4. Conclusions

In this paper, the close relationship between thermodynamic and structural data in the Se–Te system has been emphasized by means of a novel ‘regular solution model with multiple connectivity’. This model differs from the regular solution model in two ways. The connectivity of the atoms is explicitly taken into account in the derivation of the statistical mechanical treatment, and, in the resulting ternary system, the ‘chemical equilibrium’ between two distinguishable forms of the same element is treated. Beyond a very good representation of the thermodynamic data, the model predicts structural properties of the melt—basically the number of first neighbours—that are consistent with the experimental results. Although the description of the melt in terms of twofold- and threefold-coordinated



**Figure 7.** The number of first neighbours ( $Z_{av}^{Te}$ ) versus temperature, obtained in the quasi-chemical approximation using equations (17) and (23) (full line) compared with the experimental results from earlier work: ●: [25]; ■: [26].

species is rather crude and merits discussion [6], this simplified picture is useful for developing a statistical mechanical model. This study shows that the thermodynamic behaviour of the Se–Te system can be interpreted as the result of the competition between:

- (i) the structural changes undergone by pure tellurium as the temperature is raised, characterized by a ‘chemical equilibrium’ between  $\text{Te}^{\text{II}}$  and  $\text{Te}^{\text{III}}$  ‘species’;
- (ii) the displacement of this equilibrium on adding Se;
- (iii) (weak) negative interactions (the ordering tendency) between twofold-coordinated species and (weak) positive interactions between species with different coordination; and
- (iv) the effect of the entropy that stabilizes the melt at high temperature.

As the chemical interaction is rather weak (Se and Te are parent elements), the structural changes undergone by tellurium become predominant and are the origin of the observed thermodynamic behaviour. The general field of application of this model, or its possible variations, concerns such systems. In such cases, the thermodynamic data for the binary system can be used to probe the structure of one of the constitutive elements. The application of this model to the S–Te system, whose thermodynamic behaviour is also very complex, would be of great interest. Unfortunately, the available experimental data are too scarce for such an attempt.

## Appendix A

The quasi-chemical treatment of the model follows the same pattern as the Bragg–Williams one, with somewhat more complicated equations. The results are summarized here. The free energy and enthalpy of mixing, to be compared with equations (11) and (12), are now

written as

$$\Delta G^m = [X_3 - (1-x)(1-X_1)] \Delta G^0 + \sum_{i \neq j} \frac{1}{N} \bar{P}_{ij} W_{ij} + RT \left( \sum_i^3 X_i \ln X_i - \frac{1}{N} \ln \frac{\bar{\mu}}{\mu^*} \right) - (1-X_1) \left[ \frac{1}{N_{\text{Te}}} \bar{P}'_{23} W_{23} + RT \left( x \ln x + (1-x) \ln(1-x) - \frac{1}{N_{\text{Te}}} \ln \frac{\bar{\mu}'}{\mu^{*'}} \right) \right] \quad (\text{A1})$$

$$\Delta H^m = [X_3 - (1-x)(1-X_1)] \Delta H^0 + \sum_{i \neq j} \frac{1}{N} \bar{P}_{ij} W_{ij} - (1-X_1) \frac{1}{N_{\text{Te}}} \bar{P}'_{23} W_{23}. \quad (\text{A2})$$

The equilibrium equations corresponding to equations (15) and (16) become

$$RT \ln \frac{X_2}{X_3} = \Delta G^0 - \sum_{ij} \frac{\partial}{\partial X_2} \left( \frac{1}{N} \bar{P}_{ij} \right)_{T,P} W_{ij} + RT \frac{\partial}{\partial X_2} \left( \frac{1}{N} \ln \frac{\bar{\mu}}{\mu^*} \right)_{T,P} \quad (\text{A3})$$

$$RT \ln \frac{x}{1-x} = \Delta G^0 - \frac{\partial}{\partial x} \left( \frac{1}{N_{\text{Te}}} \bar{P}'_{23} \right)_{T,P} W_{23} + RT \frac{\partial}{\partial x} \left( \frac{1}{N_{\text{Te}}} \ln \frac{\bar{\mu}'}{\mu^{*'}} \right)_{T,P}. \quad (\text{A4})$$

In the above equations,  $P_{23}^{*'}$  is the number of Te<sup>II</sup>-Te<sup>III</sup> pairs in pure tellurium in the BW approximation:

$$\frac{1}{N_{\text{Te}}} P_{23}^{*'} = \frac{z_2 z_3 x (1-x)}{z_2 x + z_3 (1-x)} \quad (\text{A5})$$

and  $\bar{P}'_{23}$  is the number of Te<sup>II</sup>-Te<sup>III</sup> pairs in pure tellurium in the QC approximation:

$$\frac{1}{N_{\text{Te}}} \bar{P}'_{23} = \frac{2z_2 z_3 x (1-x)}{z_2 x + z_3 (1-x) + [(z_2 x + z_3 (1-x))^2 + 4z_2 z_3 x (1-x)(e^{2W_{23}/RT} - 1)]^{1/2}}. \quad (\text{A6})$$

$P_{ij}^*$  was defined earlier (equation (6)).

$\bar{P}_{ij}$  is the number of  $ij$  pairs in the quasi-chemical approximation. The different  $\bar{P}_{ij}$  are solutions of the following system of equations:

$$\begin{cases} \frac{(\bar{P}_{12})^2}{(z_1 N_1 - \bar{P}_{12} - \bar{P}_{13})(z_2 N_2 - \bar{P}_{12} - \bar{P}_{23})} = \exp\left(-\frac{2W_{12}}{RT}\right) \\ \frac{(\bar{P}_{13})^2}{(z_1 N_1 - \bar{P}_{12} - \bar{P}_{13})(z_3 N_3 - \bar{P}_{13} - \bar{P}_{23})} = \exp\left(-\frac{2W_{13}}{RT}\right) \\ \frac{(\bar{P}_{23})^2}{(z_2 N_2 - \bar{P}_{12} - \bar{P}_{23})(z_3 N_3 - \bar{P}_{13} - \bar{P}_{23})} = \exp\left(-\frac{2W_{23}}{RT}\right). \end{cases} \quad (\text{A7})$$

$(R/N_{\text{Te}}) \ln(\bar{\mu}'/\mu^{*'})$  is the excess-entropy term resulting from the pair permutations in pure tellurium:

$$\frac{\bar{\mu}'}{\mu^{*'}} = \frac{[\frac{1}{2}(z_2 N_2' + P_{23}^{*'})]! (\frac{1}{2} P_{23}^{*'})! (\frac{1}{2} P_{23}^{*'})! [\frac{1}{2}(z_3 N_3' + P_{23}^{*'})]!}{[\frac{1}{2}(z_2 N_2' + \bar{P}'_{23})]! (\frac{1}{2} \bar{P}'_{23})! (\frac{1}{2} \bar{P}'_{23})! [\frac{1}{2}(z_3 N_3' + \bar{P}'_{23})]!}. \quad (\text{A8})$$

$(R/N) \ln(\bar{\mu}/\mu^*)$  is the excess-entropy term resulting from the pair permutations in the alloy:

$$\frac{\bar{\mu}}{\mu^*} = \frac{(\frac{1}{2} P_{12}^*)! (\frac{1}{2} P_{12}^*)! [\frac{1}{2}(z_1 N_1 + P_{12}^* + P_{13}^*)]! (\frac{1}{2} P_{13}^*)! (\frac{1}{2} P_{13}^*)!}{(\frac{1}{2} \bar{P}_{12})! (\frac{1}{2} \bar{P}_{12})! [\frac{1}{2}(z_1 N_1 + \bar{P}_{12} + \bar{P}_{13})]! (\frac{1}{2} \bar{P}_{13})! (\frac{1}{2} \bar{P}_{13})!} \times \frac{[\frac{1}{2}(z_2 N_2 + P_{12}^* + P_{23}^*)]! (\frac{1}{2} P_{23}^*)! (\frac{1}{2} P_{23}^*)! [\frac{1}{2}(z_3 N_3 + P_{13}^* + P_{23}^*)]!}{[\frac{1}{2}(z_2 N_2 + \bar{P}_{12} + \bar{P}_{23})]! (\frac{1}{2} \bar{P}_{23})! (\frac{1}{2} \bar{P}_{23})! [\frac{1}{2}(z_3 N_3 + \bar{P}_{13} + \bar{P}_{23})]!}. \quad (\text{A9})$$

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