Thermodynamic Excess Functions for Quasiternary Solid Solutions of Type M (X, Y, Z) I. The System Pb (S, Te, Se)

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Dedicated to Prof. Dr. W. Müller-Warmuth on the occasion of his 65th birthday

The excess free enthalpy of quasiternary systems of type M (X, Y, Z) with two sublattices, a mixed one (X, Y, Z) and a pure one (M), will be described in two ways: (1) by the interaction parameters of the three subregularly treated quasibinary subsystems and by one ternary parameter, and (2) by the cluster energies of 10 pyramidal clusters.

It is shown that, for the spinodal miscibility gap in the special system Pb (S, Te, Se), both versions yield satisfying accordance of experiments and calculated results.

1. Introduction

In several recent papers relationships between properties of a ternary system and its three binary subsystems were discussed on a phenomenological level [1, 2, 3]. In this paper, we will use a microscopic cluster model based on four particle interactions, i.e. on interactions between one particle of the pure M-sublattice and three particles of the mixed XYZ-sublattice. Due to these pyramidal clusters our model can be applied to octahedrally, i.e. Pb(S, Te, Se), as well as to tetrahedrally coordinated quasiternary one-phase systems, as for example to As(Al, Ga, In) or to Te(Zn, Cd, Hg).

We will show that, for the case of random distribution within the mixed sublattice, the expression for the excess free enthalpy of the quasiternary solution can be splitted into contributions from the three subregularly behaving quasibinary subsystems and an additional contribution described by a ternary interaction parameter. For an ideal cluster mixture, the standard chemical potentials of all but one cluster can be estimated from the temperature dependent interaction parameters of the quasibinary subsystems. It is only the value for the "ternary" cluster MXYZ, with $X \neq Y \neq Z$, that has to be estimated from measurements on ternary mixtures. Knowing all the cluster energies, the probabilities for the clusters can be calculated and then the configuration entropy of the cluster mixture can be described as a function of the cluster probabilities. Thus, for an ideal cluster mixture the mean molar free mixing enthalpy can be calculated from the cluster energies.

For the special system $Pb(S_k Te_l Se_m)$ we will calculate the miscibility gap for spinodal demixing from the phenomenological expression as well as from the cluster expression for the free mixing enthalpy. The interaction parameters needed for the calculations will be derived from data on the quasibinary subsystems.

The scope of a description of a real mixture by a cluster model is not restricted to calculations of thermodynamic properties such as the excess free enthalpy. Moreover, such a description has the advantage of an atomistic model. It allows to calculate the probability of special atomic arrangements, as for example pairs of equal particles on adjacent lattice sites. Thus, one can illustrate by this model, for example, in which way the equilibria between clusters have to change with composition and temperature to favour demixing.

2. Experiments

2.1. Initial Substances

The binary compounds PbS, PbSe and PbTe were synthesized from the elements (purity: Pb 99.9999%; S, Se, Te 99.999%) in evacuated quartz ampoules. All compounds were purified by sublimation in dynamic vacuum: PbS and PbSe at 1173 K, PbTe at 1023 K.

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Because of these preparation conditions, our samples have a composition corresponding to minimal vapour pressure.

2.2. *X-Ray Measurements*

To determine the lattice constant of the solid solution in dependence on composition, a set of powder mixtures of different mole ratios of the pure binary components was prepared. All samples, sealed in evacuated quartz ampoules, were homogenized for 6 hours at 1373 K. Subsequently, the temperature was lowered slowly down to 1073 K and then the ampoules were quenched to room temperature by dipping in ice water.

One part of these samples was homogenized by annealing at 1000 K for up to 150 days. An other part that were to be used to determine the region of spinodal demixing was annealed for equilibration at lower temperatures ($800 \leq T/\mathrm{K} \leq 973$). In both cases the free volume of the ampoules was filled with a quartz rod to prevent any separation of the mixture by sublimation. To preserve the high temperature equilibrium composition, the ampoules were quenched in ice water. Afterwards the samples were investigated by the X-ray Guinier method. Those samples that suffered a spinodal demixing during equilibration showed a twofold set of cubic reflections. The other samples, with a single sharp reflection pattern, were used to find a description for the composition dependence of the cubic lattice constant $a(l, m)$ covering the whole existence region of the quasiternary solid solution $Pb(S_k Te_l Se_m)$. For the quantitative description we use a polynomial with 8 coefficients:

$$a(l,m) = (A + B \cdot l) + (C + D \cdot l)\, m + (E + F \cdot l)\, m^2 + (G + H \cdot l)\, m^3 \qquad (1)$$

with

Coeff.	A	B	C	D	E	F	G	H
Coeff./pm	646.22	−33.63	−39.68	−29.45	−30.46	71.05	17.60	−36.46

To determine these coefficients, more than 100 samples, each with a homogeneous composition, were evaluated. The composition of most of these high temperature samples was situated in that region ($m \leq 0.4$) of the phase triangle where, at lower temperatures, a spinodal miscibility gap is to be expected.

The polynomial (1) was used to obtain information on the equilibrium compositions of those samples that separated by equilibration into two solid solutions of different composition. Additional information was obtained from measurements by an electron microprobe. Because of the formation of narrow lamellas during spinodal decomposition, the accuracy of the measurement of the composition of the two solid solutions is not good enough for an exact quantitative determination of the tie lines. But the measurements with the electorn microprobe show that, on the average, the selenide mole fraction m is somewhat higher on the PbS rich side than on the PbTe rich side of a tie line. Therefrom we know that the real tie lines will show a small negative slope, which is the higher, the higher the selenide mole fraction of the overall composition of the equilibrated sample ($\Delta m \leq 0.03$).

To determine approximate values for the spinodal miscibility gap, we neglect this small slope and take a tie line as a horizontal line through the point corresponding to the overall composition of the equilibrated sample. Then, knowing the selenide mole fraction of this point, we can calculate the composition of the endpoints of this approximate tie line by means of (1) from the measured lattice constants. As the "iso lattice constant lines" run approximately at right angle to the tie lines, these calculated equilibrium points must lie on the PbTe side somewhat above, and on the PbS side somewhat below the endpoints of the real tie line. Thus, the equilibrium curve for the spinodal miscibility gap has to run on the PbS side somewhat above and on the PbTe side somewhat below those points that were determined from the lattice constants by use of the above mentioned approximation. In Figs. 1(a)–(c) and Figs. 2(a)–(c) these points are shown together with the tie line field and with the equilibrium curve that was calculated either from the experimentally determined interaction parameters of the quasibinary subsystems and one adjusted ternary parameter (Fig. 1), or by use of the cluster model (Fig. 2) that will be described in Sect. 3.2. Fig. 1 additionally shows the calculated spinodal curve separating the instable from the stable region.

3. Theoretical Considerations

3.1. *The Mean Molar Excess Free Enthalpy*

To calculate the equilibrium curve of a spinodal miscibility gap, the excess free enthalpy of the considered phase has to be known as a function of the composition.

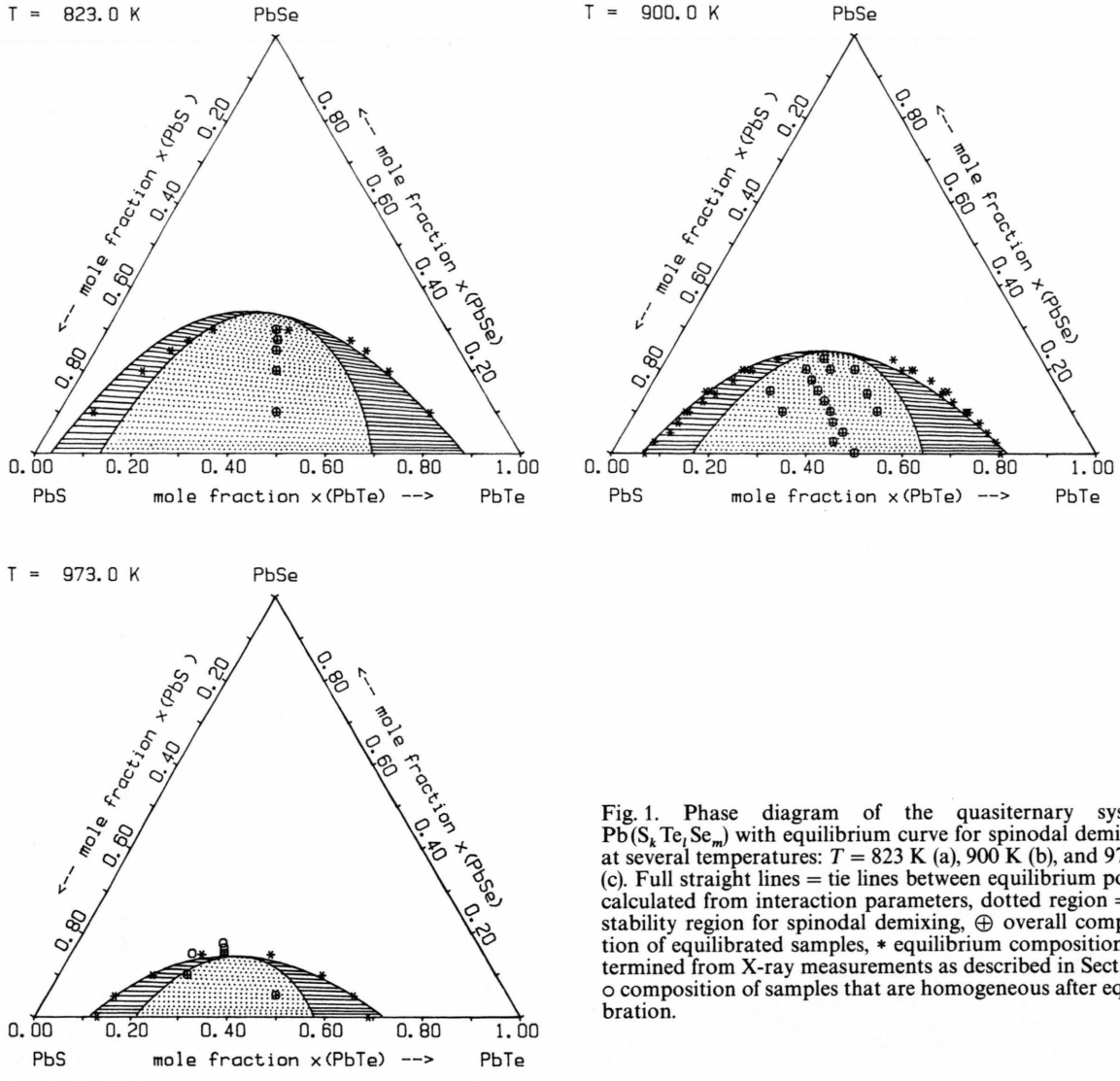

Fig. 1. Phase diagram of the quasiternary system $Pb(S_k Te_l Se_m)$ with equilibrium curve for spinodal demixing at several temperatures: $T = 823$ K (a), 900 K (b), and 973 K (c). Full straight lines = tie lines between equilibrium points calculated from interaction parameters, dotted region = instability region for spinodal demixing, ⊕ overall composition of equilibrated samples, * equilibrium composition determined from X-ray measurements as described in Sect. 2.2, o composition of samples that are homogeneous after equilibration.

By definition, regular quasibinary systems $M(X_{1-y}Y_y)$ are systems in which the excess entropy can be neglected. Thus, the excess free enthalpy is equal to the excess enthalpy expressed by an interaction parameter a_{XY} that may depend on the mole fraction y of the component MY:

$$g^E_{M(XY)} \approx h^E_{M(XY)} = (1-y)\,y \cdot a_{XY}(y). \tag{2}$$

A regular quasiternary system $M(X_k Y_l Z_m)$ is correlated to three such quasibinary subsystems $M(X_{1-y}Y_y)$, $M(Y_{1-z}Z_z)$ and $M(Z_{1-x}X_x)$. The mole fractions for the binary components MX, MY and MZ in the quasiternary system are k, l, and m, those in the quasibinary subsystems are x, y, and z. The simplest expression for the mean molar excess free enthalpy of a strict regular quasiternary system is [4]

$$g^E = k\,l\,a_{XY} + l\,m\,a_{YZ} + m\,k\,a_{ZX}. \tag{3}$$

Often, an additional ternary term $k\,l\,m\,a_{XYZ}$ is added to the three terms of (3) [5].

By extrapolation onto one of the quasibinary edges of the phase triangle, the expression for the excess free enthalpy of the quasiternary system, (3), changes to the corresponding function (2) of the quasibinary sub-

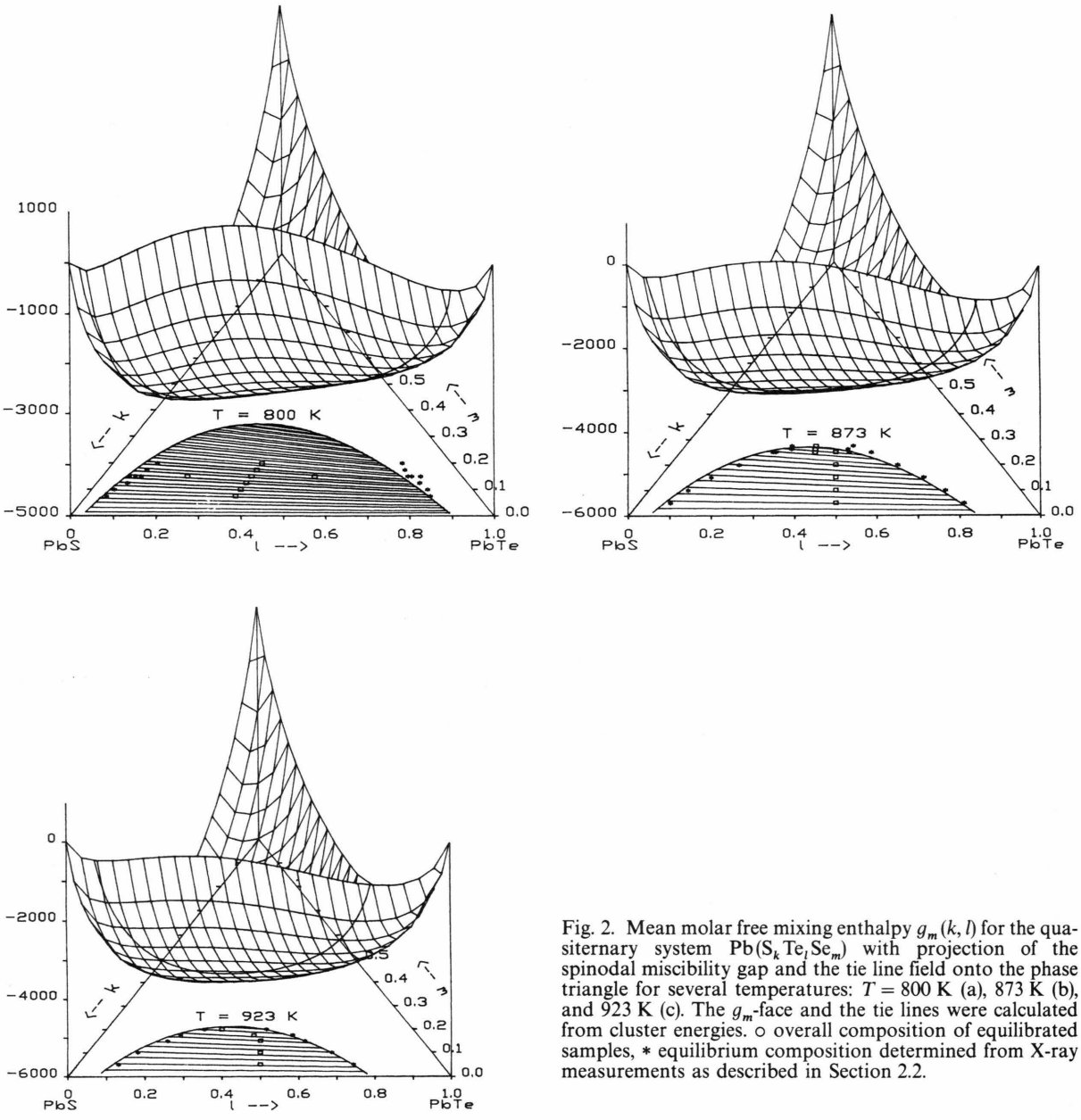

Fig. 2. Mean molar free mixing enthalpy $g_m(k, l)$ for the quasiternary system $Pb(S_k Te_l Se_m)$ with projection of the spinodal miscibility gap and the tie line field onto the phase triangle for several temperatures: $T = 800$ K (a), 873 K (b), and 923 K (c). The g_m-face and the tie lines were calculated from cluster energies. o overall composition of equilibrated samples, * equilibrium composition determined from X-ray measurements as described in Section 2.2.

system concerned. Thus, the interaction parameters in (3) are identical with those determined for the quasibinary subsystems.

In a somewhat other description a given ternary composition (k, l) can be characterized by corresponding binary compositions in such a way that the ternary mole fractions of the components A and B show the same relation as the binary mole fractions of the same components $(A, B \in \{MX, MY, MZ\})$; e.g. for the system $M(Z_{1-x}, X_x)$:

$$x = k/(1 - l); \quad 1 - x = m/(1 - l). \tag{4}$$

With these relations the mean molar excess free enthalpy g^E of a quasiternary system, described by (3), can be given as weighted sum of the $g^E_{M(AB)}$ functions

of the quasibinary subsystems [6, 7]:

$$g^{E} = (1-m)^2\, g^{E}_{M(XY)}(y) + (1-k)^2\, g^{E}_{M(YZ)}(z) + (1-l)^2\, g^{E}_{M(ZX)}(x). \quad (5)$$

If the ternary g^E function is known, the activity coefficients that are needed for the calculation of the chemical potentials of the quasibinary components ($\mu_i = \mu_{0i} + RT\ln x_i + RT\ln\gamma_i$) can be derived:

$$RT\ln\gamma_{MX} = g^{E} - l\left(\frac{\partial g^{E}}{\partial l}\right)_m - m\left(\frac{\partial g^{E}}{\partial m}\right)_l, \quad (6)$$

$$RT\ln\gamma_{MY} = g^{E} + (1-l)\left(\frac{\partial g^{E}}{\partial l}\right)_m - m\left(\frac{\partial g^{E}}{\partial m}\right)_l, \quad (7)$$

$$RT\ln\gamma_{MZ} = g^{E} - l\left(\frac{\partial g^{E}}{\partial l}\right)_m + (1-m)\left(\frac{\partial g^{E}}{\partial m}\right)_l. \quad (8)$$

3.2. The Cluster Model

3.2.1. Description of Pyramidal Clusters

A justification for a special form of the g^E function and for the dependence of the interaction parameters on composition can be derived from a cluster model describing the energy relations on an atomic scale. We will use four-particle clusters to describe the thermodynamics of solid solutions with a pure M lattice and a mixed anion lattice consisting of three different anions X, Y and Z. The basic clusters are threesided pyramids with three particles of one sublattice at the base plane and one particle of the other sublattice at the apex of the pyramid [8]. These clusters can be used for the description of tetrahedrally coordinated lattices such as zincblende (ZB) or wurtzite (WU) as well as for the octahedrally coordinated lattices such as the rocksalt lattice (RS). Depending on the lattice type L, a number f_L of clusters have always one common M particle.

$$f_{ZB} = f_{WU} = 4; \quad f_{RS} = 8. \quad (9)$$

In Table 1 the 10 differently composed clusters are listed together with the degeneracy β_i of the given cluster type i. In the representation of the clusters the specification of the M particle is omitted.

3.2.2. Energies and Probabilities of Clusters

If the energies ε_i and the probabilities $\beta_i y_i$ of all clusters with M at their apex are known, the molar energy of the solid solution $M(X_k Y_l Z_{(1-k-l)})$ can be calculated by

$$E_{XYZ} = N_A f_L \sum_{i=1}^{10} \varepsilon_i \beta_i y_i. \quad (10)$$

Alternatively this energy can also be expressed by the energies of those pyramidal clusters that have an X, Y, or Z particle at their apex:

$$E_M = N_A f_L [k\,\varepsilon_{XMMM} + l\,\varepsilon_{YMMM} + (1-k-l)\,\varepsilon_{ZMMM}]. \quad (11)$$

With the concept of molar averaged cluster energies [8]

$$\langle E_i\rangle = \tfrac{1}{2} N_A [\varepsilon_i + \tfrac{1}{3}(t_i^X \varepsilon_{XMMM} + t_i^Y \varepsilon_{YMMM} + t_i^Z \varepsilon_{ZMMM})] \quad (12)$$

(t_i^S is the number of S particles in a cluster of type i with $S \in \{X, Y, Z\}$), both ways of description can be combined. Thus, the molar energy of a solid solution crystallizing with lattice L is given by

$$E_L = f_L \sum_{i=1}^{10} \langle E_i\rangle \beta_i y_i. \quad (13)$$

Within the scope of the random distribution assumption, the occurrence probability of a cluster of type i is determined by the probabilities that given sites in the randomly mixed anion sublattice are occupied by X, Y, or Z. In this case, the individual cluster probabilities y_i can be calculated easily from the mole fractions k and l:

$$y_i = k^{t_i^X} l^{t_i^Y} (1-k-l)^{t_i^Z}. \quad (14)$$

If the sum in (13) is evaluated, one obtains a polynomial equation with terms $k^a l^b \Omega_{ab}$, where $a, b \in \{0, 1, 2, 3\}$ and $a + b \leq 3$ [9]. The Ω_{ab} terms represent linear functions of the cluster energies.

Table. 1. Representation of clusters.

No. i	1	2	3	4	5	6	7	8	9	10
Cluster i	XXX	XXY	XYY	YYY	YYZ	YZZ	ZZZ	ZZX	ZXX	XYZ
β_i	1	3	3	1	3	3	1	3	3	6

E_L is taken as approximately equal to the mean molar enthalpy of the quasiternary mixture:

$$E_L \approx h(k,l) = h_0(k,l) + h^E(k,l). \tag{15}$$

The mean molar standard enthalpy $h_0(k,l)$ of the quasiternary solid solution can be described by those Ω_{ab} terms that refer to the pure binary components, i.e. by those that contain at least one 0 in their index:

$$h_0(k,l) = k\,h(1,0) + l\,h(0,1) + (1-k-l)\,h(0,0) \tag{16}$$

$$= f_L[k(\Omega_{30} + \Omega_{20} + \Omega_{10} + \Omega_{00}) + l(\Omega_{03} + \Omega_{02} + \Omega_{01}) + (1-k-l)\,\Omega_{00}] \tag{17}$$

$$= f_L(k\langle E_1\rangle + l\langle E_4\rangle + (1-k-l)\langle E_7\rangle). \tag{18}$$

It turns out to be possible to separate the mean molar excess enthalpy into four terms: three terms describing the behaviour of the quasibinary subsystems and one term describing the very ternary interactions:

$$\begin{aligned} h^E(k,l) &= h(k,l) - h_0(k,l) \\ &= k\,l[\alpha_{XY} + l\,\beta_{XY}] \\ &\quad + l(1-k-l)[\alpha_{YZ} + (1-k-l)\,\beta_{YZ}] \\ &\quad + (1-k-l)\,k[\alpha_{ZX} + k\,\beta_{ZX}] \\ &\quad + k\,l(1-k-l)\,\Gamma. \end{aligned} \tag{19}$$

Considering that regular systems do not show any excess entropy, (19) reveals the same structure as (3), if in the latter a ternary term is included. In (19) the terms enclosed in square brackets describe the interaction parameters for the quasibinary subsystems. The equation shows that, for this model based on four particle interactions, the binary interaction parameters depend linearly on the mole fractions. The interaction parameters are linear combinations of the averaged cluster energies:

$$\alpha_{XY} = f_L(-2\langle E_1\rangle + 3\langle E_2\rangle - \langle E_4\rangle), \tag{20}$$

$$\beta_{XY} = f_L(\langle E_1\rangle - 3\langle E_2\rangle + 3\langle E_3\rangle - \langle E_4\rangle), \tag{21}$$

$$\alpha_{YZ} = f_L(-2\langle E_4\rangle + 3\langle E_5\rangle - \langle E_7\rangle), \tag{22}$$

$$\beta_{YZ} = f_L(\langle E_4\rangle - 3\langle E_5\rangle + 3\langle E_6\rangle - \langle E_7\rangle), \tag{23}$$

$$\alpha_{ZX} = f_L(-2\langle E_7\rangle + 3\langle E_8\rangle - \langle E_1\rangle), \tag{24}$$

$$\beta_{ZX} = f_L(\langle E_7\rangle - 3\langle E_8\rangle + 3\langle E_9\rangle - \langle E_1\rangle), \tag{25}$$

$$\Gamma = f_L(-\langle E_1\rangle + 3\langle E_2\rangle - \langle E_4\rangle + 3\langle E_5\rangle - \langle E_7\rangle + 3\langle E_8\rangle - 6\langle E_{10}\rangle). \tag{26}$$

If the description is not to be restricted to regular systems, the interaction parameters have to be considered as temperature functions ($\alpha(T) = \alpha - T\sigma$, $\beta(T) = \beta - T\tau$ [10]). In such cases the cluster energies also have to be taken as functions of the temperature. They can be identified with the standard chemical potentials of the individual clusters in an ideal mixture of pyramidal clusters [8]:

$$\langle E_i(T)\rangle = \mu_i^0 = H_i^0 - T\,S_i^0. \tag{27}$$

If both the interaction parameters and the standard free enthalpies of the pure binary components are known ($g_0(MX) = f_L\langle E_1\rangle$, $g_0(MY) = f_L\langle E_4\rangle$, $g_0(MZ) = f_L\langle E_7\rangle$ [8]), then we have 10 independent equations from which the 10 cluster energies can be calculated. As the derivation of the set of equations (20–26) was based on the random distribution assumption, the calculated cluster energies are good approximations only for those solid solutions that do not deviate too much from ideal behaviour.

The probabilities of the clusters are correlated by three balance equations:

$$\sum_{i=1}^{10} \beta_i y_i = 1, \tag{28}$$

$$\frac{1}{3}\sum_{i=1}^{10} \beta_i y_i t_i^X = k, \tag{29}$$

$$\frac{1}{3}\sum_{i=1}^{10} \beta_i y_i t_i^Y = l. \tag{30}$$

Furthermore, two indepenent cluster exchange reactions [11] are correlated to each of the three quasibinary subsystems. For example for the system $M(X_{1-y}Y_y)$ these reactions are

$$2\,MXYY \rightarrow MYYY + MXXY, \quad (r\,2)$$

$$2\,MXXY \rightarrow MXXX + MXYY. \quad (r\,3)$$

Moreover, one can formulate one independent additional reaction that includes the ternary cluster MXYZ, for example

$$2\,MXYZ \rightarrow MXZZ + MXYY. \quad (r\,10)$$

In thermodynamic equilibrium the cluster probabilities are determined by the standard free enthalpies $\Delta_{ri}G_0$ of the set of 7 independent cluster reactions. Each of the $\Delta_{ri}G_0$ terms is composed of the averaged cluster energies $\langle E_i(T)\rangle$ according to the stoichiometric coefficients v_i of the clusters i in the exchange reaction ($r\,i$):

$$\Delta_{ri}G_0 = \sum v_i\langle E_i\rangle = -R\,T\ln\prod_i(\beta_i y_i)^{v_i}. \tag{31}$$

With these 3 balance and 7 equilibrium equations the probabilities of all clusters can be calculated in dependence on the cluster energies and on the composition.

3.2.3. Configuration Entropy of a Cluster Mixture

To calculate the configuration entropy we will follow arguments of Kikuchi [12] and Ziman [13]. The applied procedures are totally equivalent to those described in [11].

With N_L as the number of lattice sites per sublattice, the number of distributions of independent pyramidal clusters would be

$$Q_{f_L}^{X,Y,Z} = \left(\frac{N_L!}{\{\Delta_{X,Y,Z}\}}\right)^{f_L} \text{ with } \{\Delta_{X,Y,Z}\} = \prod_{i=1}^{10} [(y_i N_L)!]^{\beta_i}. \quad (32)$$

The real number of distributions for a mixture of edge-linked pyramids with M particles at their apex is much smaller. The correction factor, calculated by use of the "pseudo assembly" concept [13], reads as follows:

$$\Gamma = \left(\frac{N_L!}{\{\bullet\}}\right)^{(1-z_L)} \text{ with}$$

$$\{\bullet\} = (k N_L)!\,(l N_L)!\,[(1-k-l) N_L]!. \quad (33)$$

z_L is the number of pyramids that have a common X, Y or Z particle ($z_{RS} = 24$, $z_{ZB} = z_{WU} = 12$).

With this correction factor we obtain the following expression for the molar configuration entropy of an ideal mixture of pyramidal clusters:

$$s_{conf}^{cluster} = \frac{R}{N_L} \ln (Q_{f_L}^{X,Y,Z}\,\Gamma) = \ln\left[\left(\frac{N_L!}{\{\Delta\}}\right)^{f_L}\left(\frac{N_L!}{\{\bullet\}}\right)^{1-z_L}\right]. \quad (34)$$

By application of Stirling's approximation ($\ln(y!) = y\ln(y) - y$) the molar configuration entropy can be described as

$$s_{conf}^{cluster} = s_{conf}^{ideal} + s_{conf}^{excess} \quad (35)$$

with

$$s_{conf}^{ideal} = -R \ln [k^k\, l^l\, (1-k-l)^{(1-k-l)}] \quad (36)$$

and

$$s_{conf}^{excess} = -R\left\{f_L \ln\left[\prod_{i=1}^{10} \{y_i^{(\beta_i y_i)}\}\right] - z_L \ln [k^k\, l^l (1-k-l)^{(1-k-l)}]\right\}. \quad (37)$$

This second part of $s_{conf}^{cluster}$ describes the additional entropy that results if the clusters have different energies, i.e. if the X, Y and Z particles are not randomly distributed.

3.2.4. The Mean Molar Free Enthalpy

If the cluster probabilities and energies are known as functions of temperature for a given composition, the mean molar free mixing enthalpy for a quasiternary solid solution of this composition can be calculated:

$$g_m(k,l) = g^E - T s_{conf}^{ideal} = g_0^{cluster} - g_0(k,l) - T s_{conf}^{cluster} \quad (38)$$

with

$$g_0^{cluster} = f_L \sum_{i=1}^{10} \mu_{0i} \beta_i y_i = E_L \quad (39)$$

and

$$g_0(k,l) = k\,\mu_0(MX) + l\,\mu_0(MY) + (1-k-l)\,\mu_0(MZ). \quad (40)$$

The cluster probabilities have to be calculated iteratively by solving for each composition a nonlinear system of 10 equations. The $g_m(k,l)$ values are calculated in steps of 0.01 in k and l over the whole phase triangle. To determine the equilibrium tie lines for spinodal miscibility gaps, the three equilibrium conditions between the chemical potentials of the binary components also have to be solved iteratively. The positions (′) and (″) on the $g_m(k,l)$ face at which the activity coefficients are to be determined by numerical derivation, are calculated for each iteration step by bicubic spline interpolation using the tabulated $g_m(k,l)$ grid.

4. The Solid Solution $Pb(S_k Te_l Se_{1-k-l})$

4.1. The Quasibinary Subsystems

(a) The system $Pb(Te_{1-z}Se_z)$ behaves nearly ideally. Its interaction parameter (Table 2) was calculated by Laugier [14] from experimental data measured by Steininger [15] and Grimes [16].

(b) The interaction parameters for the system $Pb(S_{1-y}Te_y)$ were determined in [17]. They are listed in Table 2.

(c) In connection with this work we determined the interaction parameters for the system $Pb(Se_{1-x}S_x)$ from the liquidus solidus data having been measured by Strauss and Harman [18]. Table 3 shows the fusion data of the binary components that we used for this calculation. The data for the azeotropic point ($T_{az} = 1349$ K, $x_{az} = 0.34$) that we derived from the

Table 2. Interaction parameters of the quasibinary subsystems.

System	α/(kJ/mol)	σ/[J/(mol · K)]	β/(kJ/mol)	τ/[J/(mol · K)]
$Pb(Se_{1-x}S_x)$	1.7	0	−0.8	0
$Pb(S_{1-y}Te_y)$	40.4	19.1	−11.6	−4.65
$Pb(Te_{1-z}Se_z)$	6.5	0	0	0

Table 3. Fusion data of the binary components.

Substance	$\Delta_F H$/(kJ/mol)	T_F/K
Pbs	19.0 [19]	1386 [19]
PbSe	33.1 [20, 21]	1358 [22]

interaction parameters, are in good accordance with the azeotropic point of the experimental liquidus solidus curves in [18].

4.2. The Quasiternary System

4.2.1. Calculations Using Interaction Parameters

One way to determine the spinodal miscibility gap in a quasiternary system is to calculate many tie lines between equilibrium points (′) and (″) by solving the system of the three equations that describe the equality of the activities for each of the three binary components:

$$x_i' \gamma_i' = x_i'' \gamma_i'' \quad \text{with} \quad i \in \{\text{PbS}, \text{PbSe}, \text{PbTe}\}, \tag{41}$$

The activity coefficients γ_i can be calculated according to (6)–(8), provided the excess free enthalpy $g^E(k, l)$ is known. As long as the system can be treated as behaving regularly, an excess entropy has not to be considered and the free excess enthalpy of the quasiternary system is given by (19). Thus, besides the interaction parameters, known from the quasibinary systems (cf. Table 2), we still need the ternary interaction parameter Γ. We start with an estimated value for this parameter, and then it will be varied until there is a good correspondence between the calculated fields of tie lines and the experimentally determined points of the phase diagram (Figs. 1(a)–(c)). Following the arguments given in Sect. 2.2, we adjusted the parameter Γ with the condition that on the PbTe side the equilibrium curve runs somewhat below and on the PbS side somewhat above the experimental points. A good accordance of the calculated equilibrium curves with the experimental points was obtained by the ternary parameter

$$\Gamma = -7.5 \text{ kJ/mol}. \tag{42}$$

Table 4. Standard formation enthalpies and entropies.

Substance	PbS	PbSe	PbTe
$\Delta_f H^0$/(kJ/mol)	−100.4 [23]	−75.3 [24]	−69.5 [24]
$\Delta_f S^0$/[J/(K · mol)]	5.4 [24]	−4.6 [24]	4.6 [24]

4.2.2. Calculations Using Cluster Energies

The standard enthalpies and entropies for the clusters No. 1–4, belonging to the subsystem Pb(S, Te), were taken from [8]. To derive the other cluster energies from (22)–(25) and (27), we used the interaction parameters of Table 2 and the literature values for the standard formation enthalpies and entropies of the pure binary components listed in Table 4. The energy for the ternary cluster PbSSeTe was determined by fitting the calculated tie lines to the experimental points.

The calculated set of cluster enthalpies and entropies is listed in Table 5.

In Sect. 3.2.2 it was explained that, in addition to the three balance equations, one needs the equilibrium conditions for 7 independent cluster reactions to calculate the probabilities for all 10 clusters. In accordance with previous definitions for the quasibinary subsystems [8], the following reactions were chosen as

Table 5. Cluster enthalpies and entropies.

Cluster (i) No. i	SSS 1	SSTe 2	STeTe 3	TeTeTe 4	TeTeSe 5	TeSeSe 6	SeSeSe 7	SeSeS 8	SeSS 9	SSeTe 10
$H^0_{(i)}$/kJ/mol	−12.55	−9.58	−8.78	−8.69	−8.66	−8.90	−9.41	−10.39	−11.47	−9.71
$S^0_{(i)}$/J/(K · mol)	−0.675	0.154	−0.008	−0.575	−0.575	−0.575	−0.575	−0.608	−0.642	−0.608

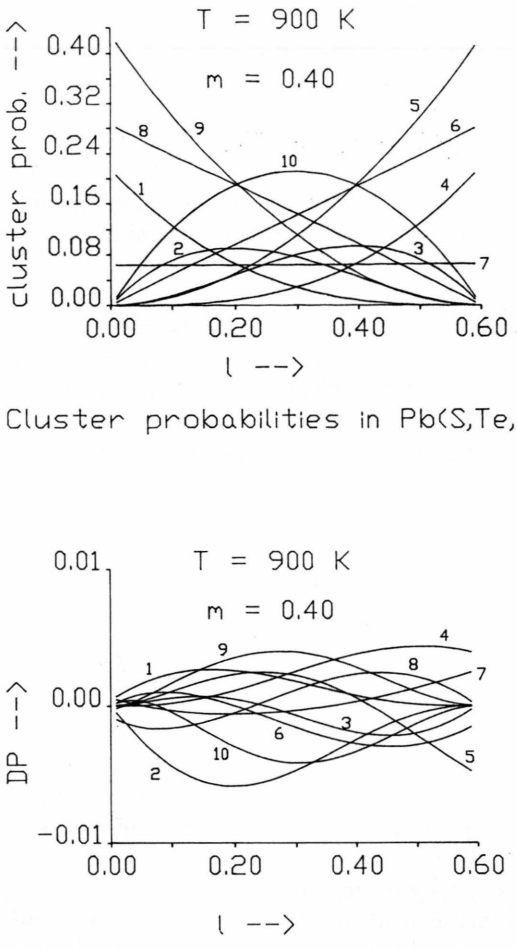

Fig. 3. Probability distribution at $T = 900$ K for the 10 clusters of the quasiternary system $Pb(S_k Te_l Se_m)$ at constant PbSe mole fraction $m = 0.4$. The numbers related to the curves correspond to the numbers of the clusters as given in Table 1. (a) absolute probabilities in dependence on the PbTe mole fraction l; (b) differences DP between probabilities in (a) and probabilities calculated with the random distribution assumption.

Table 6. Standard enthalpies and entropies for cluster reactions.

Reaction	(r 2)	(r 3)	(r 5)	(r 6)	(r 8)	(r 9)	(r 10)
$\frac{\Delta_{(ri)} H^0}{\text{J/mol}}$	−716	−2167	−270.8	−270.8	−4.2	−104.2	0.25
$\frac{\Delta_{(ri)} S^0}{\text{J/(K · mol)}}$	−0.425	−0.950	0	0	0	0	0.6

a set of independent cluster reactions. In this set, (r 10) is the only really quasiternary cluster reaction.

$$2\,\text{PbSTeTe} \rightarrow \text{PbTeTeTe} + \text{PbSSTE}, \quad (r\,2)$$
$$2\,\text{PbSSTe} \rightarrow \text{PbSSS} + \text{PbSTeTe}, \quad (r\,3)$$
$$2\,\text{PbTeSeSe} \rightarrow \text{PbSeSeSe} + \text{PbTeTeSe}, \quad (r\,5)$$
$$2\,\text{PbTeTeSe} \rightarrow \text{PbTeTeTe} + \text{PbTeSeSe}, \quad (r\,6)$$
$$2\,\text{PbSeSS} \rightarrow \text{PbSSS} + \text{PbSeSeS}, \quad (r\,8)$$
$$2\,\text{PbSeSeS} \rightarrow \text{PbSeSeSe} + \text{PbSeSS}, \quad (r\,9)$$
$$2\,\text{PbSSeTe} \rightarrow \text{PbSTeTe} + \text{PbSSeSe}. \quad (r\,10)$$

The standard enthalpies and entropies of these cluster reactions, given in Table 6, were calculated from the cluster data of Table 5.

Now, the cluster probabilities can be calculated in dependence on composition and temperature by solving the set of the three balance equations (28)–(30) and the 7 equilibrium conditions, given by (31). Figure 3 shows the composition dependence of the cluster probabilities along a quasibinary section through the phase triangle.

If the cluster probabilities are known, the equilibrium tie lines for the spinodal miscibility gap can be calculated using (38) and following the procedures described in Section 3.2.4. Figure 2 shows the $g(k, l)$ surfaces for some temperatures together with the projections of the tie line fields onto the phase triangle.

5. Conclusions

The good correlation between the experimentally determined equilibrium points and the miscibility gap, calculated from interaction parameters (cf. Fig. 1), shows that the assumption, that most of the data for the quasiternary system can be derived from the quasibinary subsystems, works very well. But, the calculations do also show that the ternary parameter Γ must not be neglected if ternary spinodal demixing is to be described.

The comparison of the phase diagrams for different temperatures shows that with decreasing temperature the extension of the spinodal miscibility gap increases and the shape of the gap becomes more and more symmetrical, i.e. the critical point of demixing changes from $x^c_{PbTe} = 0.38$, $x^c_{PbS} = 0.62$ at $T^c = 1073$ K to $x^c_{PbTe} \approx 0.32$, $x^c_{PbS} \approx 0.32$ at $T^c = 800$ K.

In Fig. 2, the tie line fields, projected from the g_m-face onto the phase triangle, were calculated from

much denser grids ($\Delta k = \Delta l = 0.01$) than those shown in the figures.

The standard chemical potentials of the clusters No. 1–9 (cf. Table 1, Table 5 and (27)) correspond very well with the interaction parameters according to (20)–(25). But the standard values for the "ternary" cluster No. 10 in Table 5, as used for the calculation of g_m, deviate distinctly from the values $H^0_{10} = -9.05$ kJ/mol and $S^0_{10} = -0.21$ J/(K · mol) that are calculated from the interaction parameters on the basis of the random distribution assumption. But in both cases, the mixed cluster PbSSeTe is less stable than one would expect for an ideal mixture of the three binary components ($[H^0_{SSS} + H^0_{SeSeSe} + H^0_{TeTeTe}]/3 = -10.2$ kJ/mol). This indicates the contribution of cluster No. 10 to the tendency of phase separation.

As to the cluster probabilities $p_i = \beta_i y_i$, Fig. 3(a) shows that, at higher PbSe contents ($m = 0.4$), the system $Pb(S_k Te_l Se_m)$ seems to behave very symmetrically with respect to the line of equimolar composition in PbS and PbTe. But a glance at the distribution of the difference probabilities in Fig. 3(b) reveals that, nevertheless, there is still a distinct unsymmetry in the behaviour of corresponding clusters, i.e. of clusters with equal PbSe content. For example the probability of the cluster PbSSTe(2) shows on the sulfide rich side a much higher deviation from the ideal distribution than the probability of the corresponding cluster PbSTeTe(3) on the telluride rich side. Furthermore, both the cluster PbTeSeSe(6) and the corresponding cluster PbSeSeS(8) yield a distinctly smaller deviation from ideality on the sulfide rich side than on the telluride rich side. The absolute deviations from the ideal distributions, however, are always rather small ($|\Delta p_i| \leq 0.006$), and moreover, the temperature dependence of the probability distributions in the region $800 \leq T/K \leq 1000$ can be neglected.

The cluster reaction ($r3$) can be interpreted as the formation of a TeTe pair from isolated Te particles in a sulfide matrix [8]. The free standard reaction enthalpy for this process can be calculated from the values listed in Table 6 ($\Delta G^0_{(r2)} = -1.3$ kJ/mol at $T = 900$ K). Compared to the other pairs, a TeTe pair in a sulfide matrix is by far the energetically most favoured pair in the investigated temperature region. Obviously, the lattice strain decreases distinctly if the relatively large isolated Te particles are situated on neighboured lattice sites. This effect is most expressed in a sulfide matrix, but even at a selenide mole fraction of $m = 0.4$ the probability of the relevant cluster type PbSTeTe(3) on the sulfide rich side is still increased compared to the random distribution in ideal mixtures (cf. Fig. 3(b)).

These investigations have shown that in quasiternary systems with one pure and one mixed sublattice one ternary interaction parameter is needed in addition to the interaction parameters of the three quasibinary subsystems to calculate the equilibrium values of spinodal demixing. With a model based on 10 differently composed pyramidal clusters one can show that approximate values for the cluster energies can be derived from the interaction parameters. Within the scope of this model the mean molar excess free enthalpy can be calculated and therefrom the phase diagram can also be derived. For the system $Pb(S_k Te_l Se_m)$ both methods work very well, but the cluster model yields additional insight in the atomic arrangement of the solid solutions.

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