Surface Properties and Concentration Fluctuations in Sn-based Molten Alloys

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A simple model based on the concept of a layered structure near the interface has been used to investigate the surface tension and surface segregation of SnPb and SnZn molten alloys. With increasing concentration of Sn, the surface tension (σ) of SnPb alloys has been found to increase, while σ of SnZn alloys decreases. σ of both systems is smaller than the ideal value $\Sigma C_i\, \sigma_i$. Our study reveals that both in SnPb and SnZn alloys the heavier atoms segregate towards the surface. The degree of segregation in SnZn alloys is greater than that in SnPb alloys. The Cahn-Hillard phenomenological model for the surface of pure liquids has been extended to binary molten mixtures and applied to the above systems. An attempt has been made to establish a link between the surface tension and the bulk properties such as concentration fluctuations in the long wavelength limit [$S_{CC}(0)$] and isothermal compressibility (χ_T). The impact of the very sensitive bulk parameter $S_{CC}(0)$ has been examined. Reasonable agreement between our model and the experiment is observed for binary molten alloys such as SnPb in which the segregation is small, while for the SnZn alloys, in which the segregation is quite large, the agreement is not satisfactory.

Key words: Surface Tension; Surface Segregation; Sn-based Alloys; Concentration Fluctuations; Order Potential.

1. Introduction

An understanding of surface properties, particularly surface segregation and surface tension, is essential in metallurgical operations and the study of catalytic activity [1–3]. Various phenomenological models, based on bond strength [4], thermodynamic parameters [5–8], phase diagram [5], surface energy [4, 9–11], microscopic electronic theories [12] etc. have been used to understand the surface segregation in terms of surface tension. Models based on the concept of layered structure near the interface [7–11, 13–16] have been found to be very successful in explaining the surface properties of binary molten alloys. Since concentration fluctuations [17–21] in the long wave length limit have helped [22–27] to understand the alloying behaviour of binary molten alloys in the bulk, attempts have been made to explain surface phenomena [28] through it.

In this paper we investigate the surface segregation and surface tension of Sn-based (SnPb and SnZn) molten alloys. An expression for the surface tension involving the surface composition has been derived. Besides, an attempt has been made to establish a link between the surface tension and bulk properties such as the concentration fluctuation in the long wave length limit ($S_{CC}(0)$ and the isothermal compressibility (χ_T). SnPb and SnZn are simple systems exhibiting simple eutectics [29]. Their excess free energy of mixing is positive, but Pb and Zn differ considerably in their surface tension (σ_{Pb} = 429 mNm^{-1}, σ_{Zn} = 772 mNm^{-1}).

Theoretical expressions are given Sect. 2, Sect. 3 deals with results and discussion and Sect. 4 with conclusions.

2. Theory

2.1. Statistical Mechanical Model

Following Prasad and Singh [7–11, 13–14], the surface grand partition function, Ξ^S, of a binary alloy, AB, can be written as

$$\Xi^S = \sum_{E_S} q_{A_S}^{N_A^S}(T)\, q_{B_S}^{N_B^S}(T) \cdot \exp\left[(\mu_A^S N_A^S + \mu_B^S N_B^S - E_S)/k_B T\right], \qquad (1)$$

where $q_{i_s}(T)$ and μ_i^S are the partition function and chemical potential of the atom i(A or B) at the surface, respectively. $N_i [= NC_i]$ and N_i^S ($\equiv NC_i^S$) represent the numbers of i(A or B) atoms in the bulk and at the surface. That total number of atoms at the surface is $N^S = \Sigma N_i^S$ and the total number of atoms in the bulk is $N = \Sigma N_i$. C_i and C_i^S are the bulk and surface concentrations, respectively. E_S is the surface configurational energy. It is assumed that A and B in the bulk and at the surface are in thermodynamic equilibrium, i.e.

$$\mu_i = \mu_i^S \tag{2}$$

μ_i refers the bulk. The surface tension of the alloy (σ) is related to the surface grand partition function Ξ^S through the relation

$$\sigma = -(k_B T/A)\ln \Xi^S = -(k_B T/\alpha N^S)\ln \Xi^S, \tag{3}$$

where A and $\alpha (= A/N^S)$ are the surface area and mean atomic surface area, respectively. In order to obtain an expression for σ through (1) and (3) one requires the suitable solution of Ξ^S. Under the regular solution approximation [7, 8], E_S is defined as the product of the order potential $W [= Z\{\varepsilon_{AB} - (\varepsilon_A + \varepsilon_B)/2\}$, where ε_{ij} are energies for i–j bonds and Z is the coordination number] and the effective number of A-B contracts at the surface. E_S is given as

$$E_S = N^S W[p C_A^S C_B^S + q\{C_A C_B^S + C_B(C_A^S - C_A)\}], \tag{4}$$

where p and q are fractions of the total number of nearest neighbours, made by an atom within its own layer and that in the adjoining layer; such that $(p + 2q) = 1$. In view of the disordered structure and the relaxation effect of the surface layer, p and q have been treated as parameters and taken as $p = 1/2$ and $q = 1/4$. It will be proper to mention that the order potential W has been assumed to be the same in the bulk and at the surface. A pair of relations for Ξ^S is obtained by the substituting E_S from (4) into (1), replacing the sum by its greatest term, differentiating with respect to C_A and equating it to zero ($\partial \Xi^S/\partial C_A^S = 0$). Application of the above obtained pair of relations for Ξ^S in (3) gives a pair of simple relations for the surface tension of the alloy:

$$\sigma = \sigma_A + (k_B T/\alpha)\ln(C_A^S/C_A) + (k_B T/\alpha)\ln(\gamma_A^S/\gamma_A) \tag{5a}$$

$$= \sigma_B + (k_B T/\alpha)\ln(C_B^S/C_B) + (k_B T/\alpha)\ln(\gamma_B^S/\gamma_B), \tag{5b}$$

where σ_i (i = A or B) is the surface tension of a pure component while γ_i and γ_i^S refer to the activity coefficients of atom i (A or B) in the bulk and at the surface, respectively.

In the frame-work of our model, γ_i and γ_i^S are related through the relation

$$\ln \gamma_i^S = p\,[\ln \gamma_i \text{ containing } C_i^S \text{ in place of } C_i] + q \ln \gamma_i. \tag{6}$$

If one has the proper expression for the bulk activity coefficient, γ_i, one can easily obtain an expression for γ_i^S by (6).

The activity coefficient for the bulk phase is expressed in the quasi-chemical model as

$$\ln \gamma_A = (Z/2)\ln[\{\beta - 1 + 2C_A\}/\{C_A(\beta + 1)\}], \tag{7a}$$

$$\ln \gamma_B = (Z/2)\ln[\{\beta + 1 - 2C_A\}/\{C_B(\beta + 1)\}], \tag{7b}$$

with

$$\beta = [1 + 4C_A C_B\{\exp(2W/Z k_B T) - 1\}]^{1/2}. \tag{8}$$

When (7) is used in (6), we obtain expressions for γ_A^S and γ_B^S. Equations (5), (6) and (7) give the surface tension of the alloy as

$$\sigma = \sigma_A + (k_B T/\alpha)\ln(C_A^S/C_A) + (Z k_B T/2\alpha) \cdot [p \ln\{(\beta^S - 1 + 2C_A^S)/(C_A^S(\beta^S + 1))\} + (q-1)\ln\{(\beta - 1 + 2C_A)/(C_A(\beta + 1)\}], \tag{9a}$$

$$= \sigma_B + (k_B T/\alpha)\ln(C_B^S/C_B) + (Z k_B T/2\alpha) \cdot [p \ln\{(\beta^S + 1 - 2C_A^S)/(C_B^S(\beta^S + 1))\} + (q-1)\ln\{(\beta + 1 - 2C_A)/(C_B(\beta + 1))\}] \tag{9b}$$

with

$$\beta^S = [1 + 4C_A^S C_B^S\{\exp(2W/Z k_B T) - 1\}]^{1/2}. \tag{10}$$

Equation (9) can be solved numerically to compute the surface tension of the alloy and the surface composition (C_i^S) as a function of the bulk concentration (C_i).

2.2. $S_{CC}(0)$ and Surface Tension

Bhatia and March [28] developed expressions for free energy contributions (F_1 and F_2) to the surface energy for liquid alloys by generalising the Cahn-Hillard phenomenological treatment of pure liquids [30, 31]. These are given as

$$F_1 = A_1 X, \tag{11}$$

$$F_2 = (Y/L^2) \tag{12}$$

with

$$X = (\partial^2 F/\partial N_A^2)_{T,P,N_B}(\Delta N_A)^2 + (\partial^2 F/\partial N_B^2)_{T,P,N_A}(\Delta N_B)^2 + 2(\partial^2 F/\partial N_A \partial N_B)(\Delta N_A \Delta N_B) \tag{13}$$

and

$$Y = b_{11}(\Delta N_A)^2 + 2b_{12}(\Delta N_A \Delta N_B) + b_{22}(\Delta N_B)^2. \tag{14}$$

F is the Helmholtz free energy, L the effective thickness of the liquid interface and V the volume. As given in the previous sub-section, N_A and N_B are the numbers of atoms A and B, respectively. ΔN_A and ΔN_B are the respective fluctuations in them, and A_1 is an accidental fluctuation, taken as equal to 1/2. The b_{ij} are constants to be eliminated later. Equations (11) and (12) give the surface tension of the alloy as

$$\sigma = (1/V)\,[A_1 XL + (1/L)\,Y]\,. \qquad (15)$$

Minimisation of σ in (15) with respect to L (($\mathrm{d}\sigma/\mathrm{d}L) = 0$) yields

$$L^2 = (Y/XA_1)\,. \qquad (16)$$

Equations (15) and (16) give σ as

$$\sigma = 2A_1 L\,(X/V)\,. \qquad (17)$$

(X/V) is expressed [17] as

$$(X/V) = (1/\chi_T N^2)\,[\Delta N + N(\Delta C)\,\delta]^2 + (1/V)\,(\partial^2 G/\partial C^2)\,(\Delta C)^2, \qquad (18)$$

where G is the Gibb's free energy for the volume V, χ_T is the isothermal compressibility of the alloy and δ is the dilatation factor. These are given as

$$\chi_T = -\,(1/V)\,(\partial V/\partial P)_{T,N,C}, \qquad (19)$$

$$\delta = (1/V)\,(\partial V/\partial P)_{T,P,N} = (V_A - V_B)/(C_A V_A + C_B V_B)\,. \qquad (20)$$

V_A and V_B are partial molar volumes of A and B. Furthermore,

$$\Delta N = \Delta N_A + \Delta N_B \qquad (21)$$

and

$$\Delta C = N^{-1}\,[C_B\,\Delta N_A - C_A\,\Delta N_B)\,. \qquad (22)$$

One finds from (17) and (18)

$$\sigma \sim (2A_1 L/\chi_T N^2)\,[\{\Delta N + N(\Delta C)\,\delta\}^2 + (\chi_T N^2/V)\,(\partial^2 G/\partial C^2)_{T,P,N}\,(\Delta C)^2]\,. \qquad (23)$$

Because of the presence of ΔC, the evaluation of σ from the above equation is difficult. ΔC can be determined by minimising σ with respect to ΔC [$\partial\sigma/\partial\,\Delta C) = 0$] a procedure similar to $(\partial\sigma/\partial L) = 0$. L has been assumed constant. We get ΔC as

$$\Delta C = [(-\,\delta/\chi_T)/\{(1/V)\,(\partial^2 G/\partial C^2) + (\delta^2/\chi_T)\}]\,(\Delta N/N)\,. \qquad (24)$$

Substitution of (24) in (23) with the conditions [24, 26–27]

$A \sim (1/2)$,
$\Delta N \sim N$,
$\Delta N_i \sim N_i$, (i = A or B),
$\Delta C \sim \ll 1$

gives σ as

$$\sigma \sim (L/\chi_T)\,[1 + \{\delta^2\,S_{CC}(0)/N k_B T \chi_T\}]^{-1}. \qquad (25)$$

It is proper to mention that the concentration fluctuations in the long wave length limit [$S_{CC}(0)$] [17] has been introduced in place of $(\partial^2 G/\partial C^2)$ through the relation

$$S_{CC}(0) = N k_B\,T\,[\partial^2 G/\partial C^2]^{-1}{}_{T,P,N}\,. \qquad (26)$$

By making use of standard thermodynamic relations, the above equation can also be written in the form

$$S_{CC}(0) = C_B\,a_A\,[\partial a_A/\partial C_A]^{-1}{}_{T,P,N} = C_A\,a_B\,[\partial a_B/\partial C_B]^{-1}{}_{T,P,N}\,. \qquad (27)$$

a_i is the activity of atom i(A or B)

Equation (27) is customarily used to obtain experimental values of $S_{CC}(0)$ from measured activity data or free energy of mixing data.

3. Results and Discussion

The surface tension (σ) and surface compositions (C_i^S) of SnPb and SnZn molten alloys have been computed as functions of the bulk concentrations (C_i) by solving (9) numerically. Experimental [32–33] values of the surface tension of the pure components σ_i (i = Sn, Pb, Zn) are

at T = 823 K: [32]:	at T = 723 K: [33]:
$\sigma_{Sn} = 545.698$ mNm^{-1},	$\sigma_{Sn} = 533.33$ mNm^{-1},
$\sigma_{Pb} = 429.032$ mNm^{-1},	$\sigma_{Zn} = 783.33$ mNm^{-1}.

As discussed earlier, $p = 1/2$, $q = 1/4$. The mean atomic surface area [α] has been calculated through the relation [34]

$$\alpha = 1.102\,N^{-2/3}\,\Omega^{2/3}. \qquad (28)$$

Ω is the volume of the alloy. Experimental [35] values of Ω have been taken for the SnPb-system, whereas for the SnZn system linear values of Ω [$C_{Sn}\,\Omega_{Sn} + C_{Zn}\,\Omega_{Zn}$)] have been taken. The order potential W has been calculated through the simple relation [26, 36]

$$(G_M^{XS}/N k_B T) = \ln 2^{Z/2}[1 + \exp(-W/Z k_B T)]^{-Z/2}. \qquad (29)$$

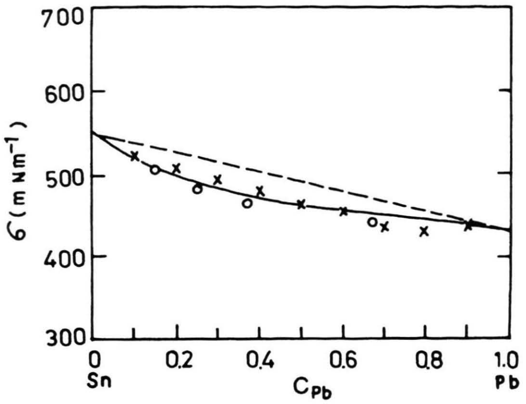

Fig. 1. Surface tension, σ, of PbSn liquid alloys at 823 K as a function of the bulk concentration, of Pb; ——— theory (9), × × × theory (25) and o o o experiment [32].

G_M^{XS} is the excess free energy of mixing. The co-ordination number Z, is equal to 10. The observed [29] values of G_M^{XS} for SnPb yield $W = 1.15\ k_B T$. For SnZn, W becomes $0.985\ k_B T$. The temperature dependence of W, has been ignored.

The computed values of the surface tension of the SnPb system at $W = 1.15\ k_B T$ are plotted as a function of the bulk concentration of Pb in Figure 1. We observe that the theoretical results agree well with the experimental [32] ones. But σ for the SnZn molten alloys, at $W = 0.985\ k_B T$, as a function of the bulk concentration of Sn deviates considerably from the experiment [33]. In view of this disagreement, W for the SnZn system has been treated as parameter and fixed as equal to $2.7\ k_B T$. It is observed that there is good agreement between the computed results of σ with $W = 2.7\ k_B T$ (Fig. 2) and the experiment [33]. C_i^S vs. C_i is presented in Figs. 3 and 4 for the respective SnPb and SnZn systems along with calculated values by other workers [15, 37]. It is clear from Figs. 3 and 4 that Pb atoms segregate to the surface in the SnPb system, whereas the SnZn system exhibits a segregation of Sn-atoms to the surface. The extent of segregation in the SnZn system is, of course, higher than that in the SnPb system. Even for small bulk compositions of Sn, the surface is quite enriched with Sn-atoms. For the bulk composition $Sn_{0.1}Zn_{0.9}$ the surface composition of the alloy becomes $Sn_{0.9}Zn_{0.1}$. In the case of SnPb, the surface composition of an alloy with the bulk composition $Sn_{0.9}Zn_{0.1}$ is $Sn_{0.636}Pb_{0.364}$. This might be due to a higher order potential W and a larger surface tension effect. The larger positive values of $(W/k_B T)$ for the SnZn system in comparison to the calculated values from (29) suggest that the inter-atomic energies at the surface differ from those in the bulk.

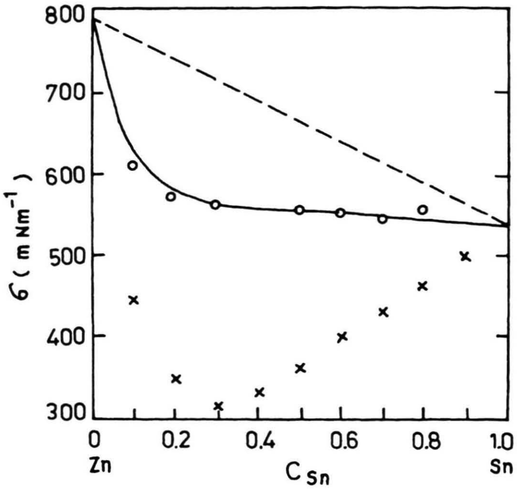

Fig. 2. Surface tension, σ, of SnZn liquid alloys at 723 K as a function of the bulk concentration, of Sn; ——— theory ((9) with W = 2.7 $k_B T$), × × × theory (25) and o o o experiment [33].

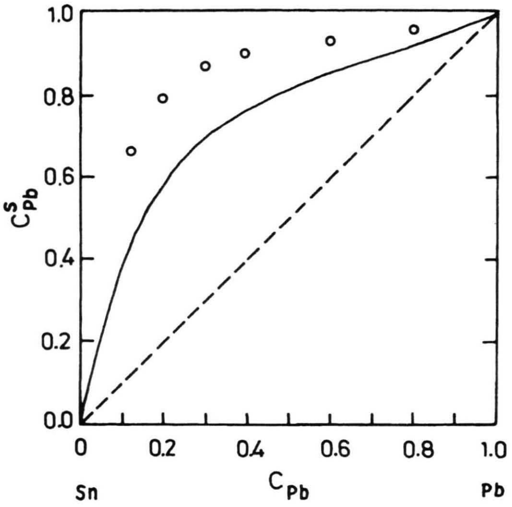

Fig. 3. Surface concentration, C^S_{Pb}, of PbSn liquid alloys at 823 K as a function of the bulk concentration C_{Pb}; ——— our theory and o o o values calculated by Yeum et al. [15].

Equation (25) has also been used to compute σ for our systems as a function of concentration. The required data for the computation are $S_{CC}(0)$, χ_T, δ and and L. $S_{CC}(0)$ for both systems have been calculated from observed [29] activity data through (27}. Experimentally [38] deter-

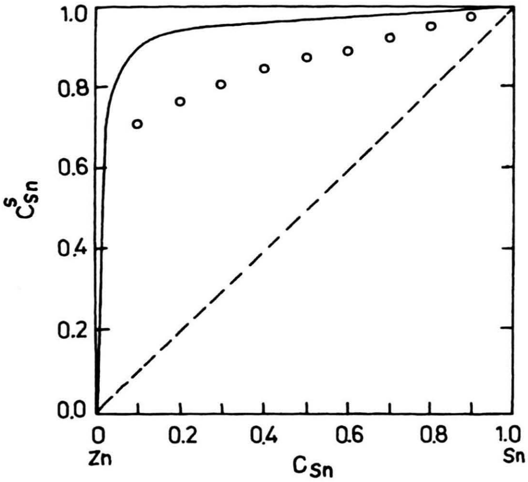

Fig. 4. Surface concentration, C^S_{Sn}, of SnZn liquid alloys at 723 K as a function of the bulk concentration, of C_{Sn}; —— our theory and o o o values calculated by Moser and Kucharski [37].

mined χ_T values have been taken, while the dilatation factor δ has been calculated by (20). The thickness (L) of the interface of the alloy has been calculated through the relation $\Sigma C_i L_i$ (i = A, B). L_i is the thickness of the interface of the pure liquid. For the calculation of L_i we have used the Cahn-Hillard phenomenological model [30, 31] of pure liquids [28]. It can be determined easily from the relation

$$\sigma_i \chi_T \sim L_i. \tag{30}$$

Our computed results for SnPb and SnZn alloys are depicted in Figs. 1 and 2, respectively. Reasonable agreement between theory and experiments is observed in the case of the SnPb system. But computed results from (25) for the SnZn system deviate considerably from (9) and experiment [33]. It may be recalled that the SnZn system is more segregating than the SnPb system. Since equation (25) contains the very sensitive parameter $S_{CC}(0)$, it will not be wise to expect this relation to give satisfactory quantitative results for systems such as SnZn, in which the segregation is quite large.

4. Conclusion

A comparative study of the concentration dependent surface tension and surface segregation of SnPb and SnZn molten alloys has been undertaken. Our theoretical investigation gives contrasting result for these systems. The surface tension of SnPb increases, whereas the surface tension of SnZn decreases with increasing concentration of Sn. The surface tension of both the systems is smaller than the ideal value $\Sigma C_i \sigma_i$. Our study reveals that Pb-atoms segregate to the surface in SnPb alloys, while Sn-atoms segregate to the surface in SnZn alloys. The extent of segregate in SnZn alloys is greater than that in SnPb alloys.

It is also found that the interatomic energies at the surface in SnZn alloys are different from those in the bulk. We have tried to investigate the impact of concentration fluctuations in the long wave length limit, $S_{CC}(0)$, on the surface tension of the above Sn-based alloys. A theoretical expression of the surface tension involving bulk parameters such as $S_{CC}(0)$ and the isothermal compressibility (χ_T) has been found to be successful to a greater extent for alloys such as SnPb, in which segregation is not so large. But it will not be wise to expect this relation to give quantitative results for alloys, such as SnZn, in which segregation is quite large. Owing to the sensitive nature of $S_{CC}(0)$, the expression might not be giving good results for the SnZn system.

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[1] P. Vander Plank and W. M. H. Sachter, J. Catal. **12,** 35 (1968) and **7,** 300 (1968).
[2] W. M. H. Sachter and P. Vander Plank, Surf. Sc. **18,** 62 (1969).
[3] H. Sinfelt, Bimetallic Catalysis: Discoveries, concept Applications, John Wiley & Sons, New York 1983.
[4] F. J. Williams and D. Nason, Surf. Sc. **45,** 377 (1974).
[5] J. J. Burton and E. S. Machlin, Phys. Rev. Lett. **37,** 1433 (1976).
[6] S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, Chem. Rev. **75,** 547 (1975).
[7] L. C. Prasad, R. N. Singh, Phys. Rev. B **44,** 13768 (1991).
[8] V. N Singh and L. C. Prasad, Indian J. Phys. **74(B),** 15 (2000)
[9] L. C. Prasad, R. N. Singh, and G. P. Singh, Phys. Chem. Liq. **27,** 179 (1994).
[10] L. C. Prasad and A. Mikula, High Temp. Mater. and Processes **19,** 61 (2000).
[11] L. C. Prasad and A. Mikula, Jr. of Alloys and Compounds **299,** 175 (2000).
[12] G. Kerker, J. L. Moran-Lopez, and K. H. Bennemann, Phys. Rev. B **15,** 638 (1977).

[13] L. C. Prasad, R. N. Singh, V. N. Singh, and G. P. Singh, Jr. of Phys. Chem. B (Amer. Chem. Soc.) **102,** 921 (1998).

[14] L. C. Prasad and R. N. Singh, Main Group Elements and Their Compounds, V. G. Das Kumar (Ed.), Narosa Publ. House, N. Delhi, 227 (1996).

[15] K. S. Yeum, R. Speiser, and D. Poirier, Metall. Trans. **20 B,** 693 (1989).

[16] D. R. Poirier and R. Speiser, Metall. Trans. **18 A,** 1156 (1987).

[17] A. B. Bhatia and D. E. Thornton, Phys. Rev. **B 2,** 3004 (1970).

[18] R. N. Singh and F. Sommer, Rep. Prog. Phys. **60,** 57 (1997).

[19] R. N. Singh, Can. J. Phys. **65,** 309 (1987).

[20] W. H. Young, Rep. Phys. **55,** 1769 (1992).

[21] V. N. Singh, L. C. Prasad, and M. Jha, J. Indian Chem. Soc. **76,** 382 (1999).

[22] R. N. Singh and F. Sommer, Z. Metallkde **83,** 533 (1992).

[23] N. H. March, Liquid Metals: Concept and Theory, University Press, Cambridge (1990).

[24] L. C. Prasad, S. K. Chatterjee, and V. N. Singh, Physica B **217,** 285 (1996).

[25] L. C. Prasad, R. N. Singh, V. N. Singh, and S. K. Chatterjee, Physica B **215,** 225 (1995).

[26] L. C. Prasad and R. N. Singh, Phys. Chem. Liq. **22,** 1 (1990).

[27] R. N. Singh and N. H. March, Intermetallic Compounds. Vol. 1 – Principles Edited by J. H. Westbrook and R. L. Fleischer, John Wiley & Sons, New York, p. 661. (1994).

[28] A. B. Bhatia and N. H. March, J. Chem. Phys. **68,** 4651 (1978).

[29] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelly, Selected Values of the Thermodynamic Properties of Binary Alloys, Metal Park, OH ASM (1973).

[30] J. W. Cahn and J. E. Hillard, J. Chem. Phys. **28,** 258 (1958).

[31] R. C. Brown and N. H. March, Phys. Repts. **24,** 77 (1976).

[32] T. P. Hoar and D. A. Melford, Trans. Faraday Soc. **53,** 315 (1957).

[33] M. Kucharski, Zesz Nauk AGH Metal, Odlewn **3,** 329 (1977).

[34] P. Laty, J. C. Joud, and P. Desre, Surf. Sc. **60,** 109 (1976).

[35] B. Predel and A. Emam, Matr. Sci. Eng. **4,** 287 (1969).

[36] R. N. Singh, I. K. Mishra, and V. N. Singh, Jr. Phys. Condens Matter **2,** 8457 (1990).

[37] Z. Moser and M. Kucharsky, Jr. Non Cryst. Solids **156–158,** 369 (1993).

[38] S. I. Filippov, N. B. Kazakov, and L. A. Pronin, Izv. VUZ Chem. Met. **9,** 8 (1966).