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Assessment of Thermodynamic and Structural Properties of AgAl Melts at 1273 K

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Abstract
The thermodynamic behavior of binary melts of AgAl molten system at 1273 K are analyzed in the framework of four-parameter model. For this, the model parameters are required which are evaluate on utilizing the experimental data of excess free energy of mixing of AgAl system at 1273 K. An excellent harmony is observed between theory and corresponding experimental data available in the literature on the basis of concentration of Ag. Again, on assuming the temperature dependence of the model parameters, the entropy of mixing and heat of mixing for AgAl melts are analyzed theoretically in the framework of four-parameter model. Further, the theoretical data of concentration fluctuations are employed to explain the short-range order parameter and diffusivity ratio of AgAl melts at 1273 K. The results reveal the ordering nature of AgAl melts at 1273 K and asymmetries in free energy of mixing and entropy of mixing, and asymmetries in excess free energy of mixing and heat of mixing for AgAl melts at 1273 K are successfully explained.

Keywords: Concentration fluctuations, four-parameter model, free energy of mixing, entropy of mixing and activity

Introduction
The AgAl alloys have potential applications due to enhanced electrical conductivity, mechanical strength, ductility, durability, corrosion resistance etc [1]. The AgAl system also known as master alloy is utilized for grain refining, hardening and enhancing the comprehensive production of other alloys. The AgAl alloys are also used as foils, sheets, plates, rods, powder, tubes etc.

The phase diagram [2] reveals that the composition dependence of the excess free energy of mixing, $\frac{G_M^{XS}}{RT}$, free energy of mixing, $\frac{G_M}{RT}$ and entropy of mixing, $\frac{S_M}{R}$ for AgAl melts 1273 K are asymmetries about the composition, C= 0.5. Again, the enthalpy of mixing, $\frac{H_M}{RT}$ versus composition isotherm represents S-shaped nature for AgAl melts at 1273 K. Further, there exist the chemical complexes Ag_2Al and Ag_3Al in the solid phase of AgAl system. The anomalous nature and potential applications of AgAl melts have drawn the attention of several investigators [1, 3-5]. However, the thermophysical properties of AgAl liquid alloys still require the theoretical investigation.

In present study, the four-parameter model, FPM [6, 7] is utilized to study the thermodynamic properties like $\frac{G_M^{XS}}{RT}$, $\frac{G_M}{RT}$, activity coefficient, γi, activity, a_i, $\frac{H_M}{RT}$ and $\frac{S_M}{R}$; and microscopic properties like concentration fluctuations, $S_{CC}(0)$ [8, 9] and short-range order parameter, α_1 [10, 11] of AgAl melts at 1273 K.

2. Formalism
The thermodynamic and structural behavior of the binary melts can be discussed by four-parameter model FPM [6] which is based on Maclaurin infinite series under suitable boundary conditions.

2.1 Thermodynamic and microscopic functions of binary melts at a given temperature:

Consider a binary molten mixture A-B containing N_A and N_B atoms of elements A and B respectively so that $N_A = NC_A$ and $N_B = NC_B$ where, $C_i (i \equiv A,B)$ indicates the concentration of the component i of the alloy.

In the framework of FPM [6], the expression for $\frac{G_M^{XS}}{RT}$ is expressed as

$$\frac{G_M^{XS}}{RT} = C_1C_2\left(a_1 + a_2C_2 + C_1C_2a_3 + C_1C_2^2a_4\right) \quad (1)$$

where, R and T are molar gas constant and absolute temperature (in K) respectively, $C_A = C$ and $C_B = 1 - C$, $a_i (i \equiv 1,2,3,4)$ are interaction parameters.

The activity coefficient of the i^{th} component of the binary alloy, $\gamma i \quad (i \equiv A, B)$ is given by

$$RT \ln \gamma_i = G_M^{XS} + (1 - C_i)\left(\frac{\partial G_M^{XS}}{\partial C_i}\right) \quad (2)$$

Equations (1) and (2) provide

$$ln\gamma_1 = C_B^2[a_1 - a_2 + 2C_Ba_2 + C_A(3C_B - 1)a_3 + 2C_AC_B(2C_B - 1)a_4] \quad (3)$$

$$ln\gamma_2 = C_A^2\left[a_1 + 2C_Ba_2 + C_B(2 - 3C_B)a_3 + C_B^2(3 - 4C_B)a_4\right] \quad (4)$$

For the binary melts, γ_i and $a_i \quad (i \equiv A, B)$ are related as

$$\Upsilon_i = \frac{a_i}{C_i} \quad (5)$$

For i^{th} component $(i \equiv A, B)$ of the binary melt, the excess entropy, S_i^{XS} is expressed as [12]

$$\frac{S_i^{XS}}{R} = -\ln \gamma_i - T\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P \quad (6)$$

The equations (3), (4) and (6) provide

$$\frac{S_A^{XS}}{R} = -C_B^2\left[\left(a_1 + a_1'T\right) + (2C_B - 1)\left(a_2 + a_2'T\right) + (1 - C_B)(3C_B - 1)\left(a_3 + a_3'T\right) + 2C_B(1 - C_B)(2C_B - 1)\left(a_4 + a_4'T\right)\right] \quad (7a)$$

$$\frac{S_B^{XS}}{R} = -C_A^2\left[\left(a_1 + a_1'T\right) + 2C_B\left(a_2 + a_2'T\right) + C_B(2 - 3C_B)\left(a_3 + a_3'T\right) + C_B^2(3 - 4C_B)\left(a_4 + a_4'T\right)\right] \quad (7b)$$

where a prime on a_1, a_2, a_3 and a_4 denotes the temperature derivative of interaction parameters i.e. $\frac{\partial a_i}{\partial T}$ $(i \equiv 1,2,3,4)$

For a binary melt, the excess entropy of mixing, S_M^{XS} is represented by

$$\frac{S_M^{XS}}{R} = C_A\frac{S_A^{XS}}{R} + C_B\frac{S_B^{XS}}{R} \quad (8)$$

Now the entropy of mixing, S_M of the binary melt is expressed as

$$\frac{S_M}{R} = \frac{S_M^{XS}}{R} + \frac{S_M^{id}}{R}$$

$$\frac{S_M}{R} = \frac{S_M^{XS}}{R} - \left(C_A \ln C_A + C_B \ln C_B\right) \tag{9}$$

The enthalpy of mixing, H_M of a binary alloy is expressed as

$$H_M = G_M^{XS} - T\left[\frac{\partial G_M^{XS}}{\partial T}\right] \tag{10}$$

$$\frac{H_M}{RT} = TC_AC_B\left[a_1' + C_Ba_2' + C_AC_Ba_3' + C_AC_B^2a_4'\right] \tag{11}$$

The enthalpy of mixing can also be represented as

$$\frac{H_M}{RT} = \frac{G_M^{XS}}{RT} + \frac{S_M^{XS}}{RT} \tag{12}$$

The microscopic function such as $S_{CC}(0)$ [8,9] is found to be successful to analyze the nature of atomic interactions in a binary system. For segregating nature of the binary melts, $Scc(0) > Scc^{(id)}(0)$, where like atoms (A-A or B-B) interaction takes place in the molten system. Similarly, for ordering nature of the binary melts, $Scc(0) < Scc^{(id)}(0)$ where unlike atoms (A-B) interaction takes place in the molten system [9]. The analytical expression for $S_{CC}(0)$ is illustrated as [9]

$$S_{CC}(0) = RT\left[\frac{\partial G_M}{\partial c^2}\right]^{-1}_{T,P,N} \tag{13}$$

Where, G_M is expressed as

$$G_M = G_M^{XS} + G_M^{id}$$

$$G_M = G_M^{XS} + RT\left[C_A \ln C_A + C_A \ln C_A\right]$$

$$\frac{G_M}{RT} = \frac{G_M^{XS}}{RT} + \left[C_A \ln C_A + C_A \ln C_A\right]$$

$$\frac{G_M}{RT} = C_AC_B\left[a_1 + C_Ba_2 + C_AC_Ba_3 + C_AC_B^2a_4\right] + \left(C_A \ln C_A + C_B \ln C_B\right) \text{ (From equation (1))} \tag{14}$$

From equation (13) and (14)

$$S_{CC}(0) = \left[-2a_1 + 2(3C_A - 2)a_2 + 2(1 - 6C_A + 6C_A^2)a_3 + 2(1 - 9C_A + 18C_A^2 - 10C_A^3)a_4 + \frac{1}{C_AC_B}\right]^{-1} \tag{15}$$

In terms of activity, $S_{CC}(0)$ can be represented as

$$S_{CC}(0) = C_Ba_A\left[\frac{\partial a_1}{\partial C_A}\right]^{-1}_{T,N,P} = C_Aa_B\left[\frac{\partial a_2}{\partial C_B}\right]^{-1}_{T,N,P} \tag{16}$$

The computed values of $S_{CC}(0)$ from equation (16) are considered as the experimental data of $S_{CC}(0)$.
The ideal values of $S_{CC}(0)$ is given by

$$S_{CC}^{id}(0) = C_AC_B \tag{17}$$

The microscopic function like SRO, α_1 [9, 10, 11] explains the atomic arrangement in a molten alloy. The negative value of α_1 refers to the ordering behavior of the alloy, while the positive value of α_1 indicates the segregating character of the alloy. In terms of $S_{CC}(0)$, α_1 is expressed as

$$\alpha_1=\frac{S-1}{S(Z-1)+1} \text{ with } S=\frac{S_{CC}(0)}{S_{CC}^{id}(0)} \tag{18}$$

where, Z = coordination number, its value is usually taken as 10 during the computation of SRO.

3. Results and Discussions

The thermodynamic and microscopic properties of the AgAl melts at 1273K are explored on using the analytical equations deduced in the framework of FPM model.

3.1 Thermodynamic and microscopic functions of AgAl melts at 1273K

To compute the thermodynamic functions like $G_M^{XS}, G_M, \gamma_{(i)}, a_i, H_M, S_M$ and microscopic functions like $Scc(0)$ and α_1 of AgAl melts at 1273 K by analytical expressions, the required parameters are a_1, a_2, a_3 and a_4. The values of a_1 and a_2 are evaluated with the experimental values of activity coefficient, γ_i $(i \equiv Ag, Al)$ in the infinite dilute solution range [2] on using the relation [6].

$$a_1 = \ln \gamma_{Sn}^0 (Cu) = \frac{1}{RT} \ln \left[\frac{\partial G_M^{XS}}{\partial C_B} \right]_{C_A \to 1.0} \tag{21a}$$

$$a_2 = \ln \gamma_{Cu}^0 (Sn) - \ln \gamma_{Sn}^0 (Cu) \tag{21b}$$

$$\ln \gamma_{Cu}^0 (Sn) = a_1 + a_2 = \frac{1}{RT} \ln \left[\frac{\partial G_M^{XS}}{\partial C_A} \right]_{C_B \to 1.0} \tag{22}$$

The values of a_1 and a_2 for AgAl melts at 1273 K are – 3.0586 and 1.7375 respectively. For the evaluation of a_3 and a_4, the successive approximation approach [7,13] is utilized on using the experimental values of G_M^{XS} in the relation given below

$$\frac{G_M^{XS}}{RT} \frac{1}{C_A C_B} - a_1 - a_2 C_B = C_A C_B a_3 + C_A C_B^2 a_4 \text{ (from equation (1))} \tag{23}$$

The approximate values of a_1, a_2,a_3 and a_4 are assumed as the starting values. The values of a_1, a_2, a_3 and a_4 are slightly adjusted until a good harmony is observed between the theory and experiment for $\frac{G_M^{XS}}{RT}$ of AgAl melts at 1273 K. The best fit values of a_1,a_2,a_3 and a_4 are

a_1 = -3.0586 a_2 = 1.7375

a_3 = -3.5016 a_4 = 5.7836

It should be pointed out that the best fit values of interaction parameters are utilized for the computations of all the properties of the alloys under investigation to maintain the consistency. The equations (1) and (14) are used to determine $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ respectively of AgAl melts at 1273K. Fig.1 shows good agreement between the theory and experimental values [2] as a function

of concentration of Ag.The $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ are negative in the region, C_{Ag} = 0.1 to 0.9. The theoretical and experimental values of $\frac{G_M^{XS}}{RT}$ are minimum i.e. – 0.6357 (Theory) and - 0.6233 (Experiment) both at C_{Ag} = 0.6. The minimum values of $\frac{G_M}{RT}$ are -1.3087 (Theory) and -1.2965 (Experiment) both at C_{Ag} = 0.6.Thus, the observed asymmetries in G_M^{XS} and G_M for AgAl melts at 1273K are well reproduced.

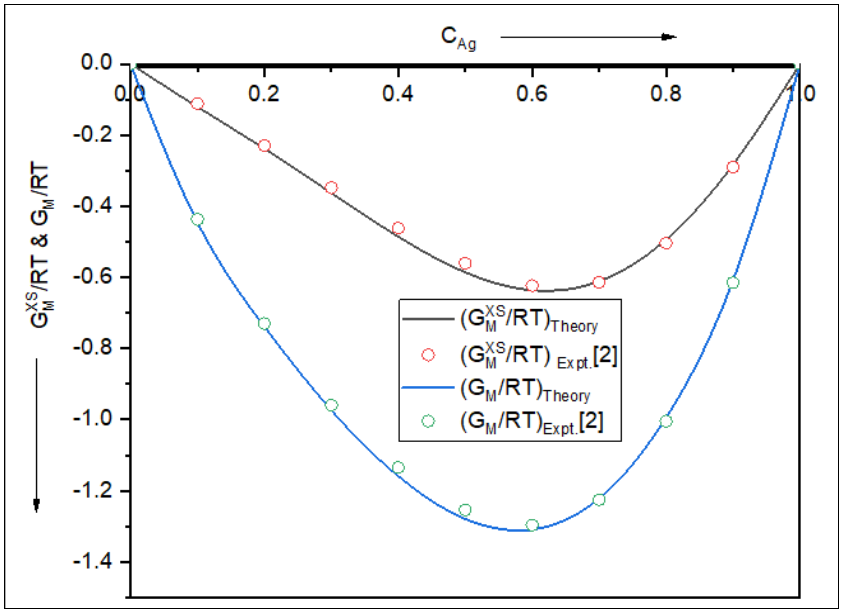

Fig 1: G_M^{XS}/RT and G_M/RT vs C_{Ag} for AgAl melts at 1273 K

The activity coefficient γ_{Ag} and γ_{Al} computed from equations (3) and (4) relative to the composition of Ag for AgAl melts at 1273K. The theoretical data of γ_{Ag} and γ_{Al} are compared with the corresponding experiment data [2] in Fig.2. The good similarities between the theory and experiment are observed.

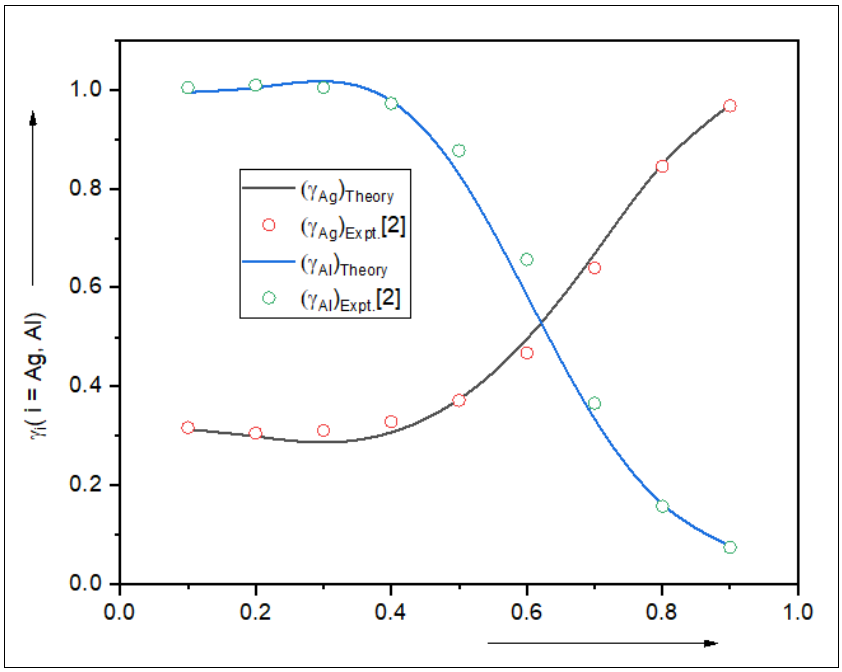

Fig 2: $2\gamma_i$ (i = Ag,Al) vs C_{Ag} for AgAl melts at 1273 K

The theoretical values of γ_{Ag} and γ_{Al} are utilized to determine the values of a_{Ag} and a_{Al} from equation (5). The comparison between the theoretical data and corresponding experimental data for a_{Ag} and a_{Al} [2] shows excellent harmony as illustrated in Fig.3. In full composition region i.e. C_{Ag} = 0.1 to 0.9, a_{Ag} and a_{Al} indicate the negative deviations from the ideal mixing behavior for AgAl melts at 1273 K. This indicates the ordering character of AgAl melts at 1273 K i.e unlike atoms (Ag-Al) interact together as nearest neighbors.

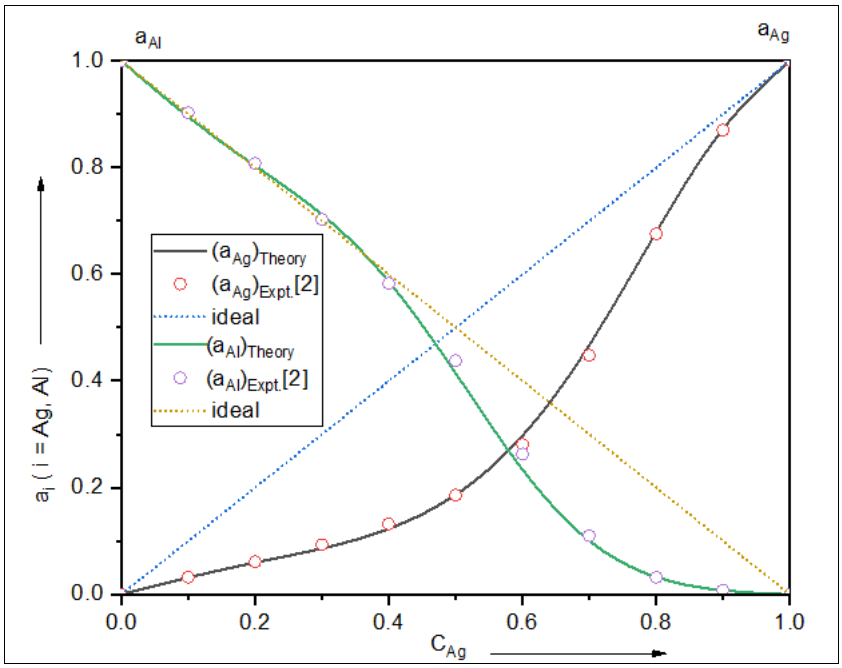

Fig 3: 3 a_i (i = Ag, Al) vs C_{Ag} for AgAl melts at 1273 K

For the determination of S_M and H_M the temperature derivatives of interaction parameters i.e. a_1`, $a_2$`, a_3`and $a_4$`are required as clear from the equations (9) and (11). The least square method is applied on using the experimental data of H_M in equation (11) to evaluate the values of a_1`,$a_2$`,a_3`and a_4. The values are:

a_1` = - 0.0046044 $a_2$` = 0.0051698
a_3` = - 0.0055490 $a_4$` = 0.0043999

The above values are utilized in equation (11) to compute the values of H_M for AgAl melts at 1273 K. In Fig.4, the theoretical values of $\frac{H_M}{RT}$ are compared with the experimental values [2] which shows a good agreement. The theoretical data of $\frac{H_M}{RT}$ in the concentration region $0 \leq C_{Ag} \leq 0.17$ are positive and negative in region $0.17 \leq C_{Ag} \leq 1.0$ with minimum value i.e. 0.580 at C_{Ag} = 0.75 while the experimental data indicate positive values of $\frac{H_M}{RT}$ in the region $0.0 \leq C_{Ag} \leq 0.2$ and negative values in the region $0.2 \leq C_{Ag} \leq 1.0$ with minimum value i.e. 0.606 at C_{Ag} = 0.7 Thus, the S-shaped nature of $\frac{H_M}{RT}$ is successfully explained.

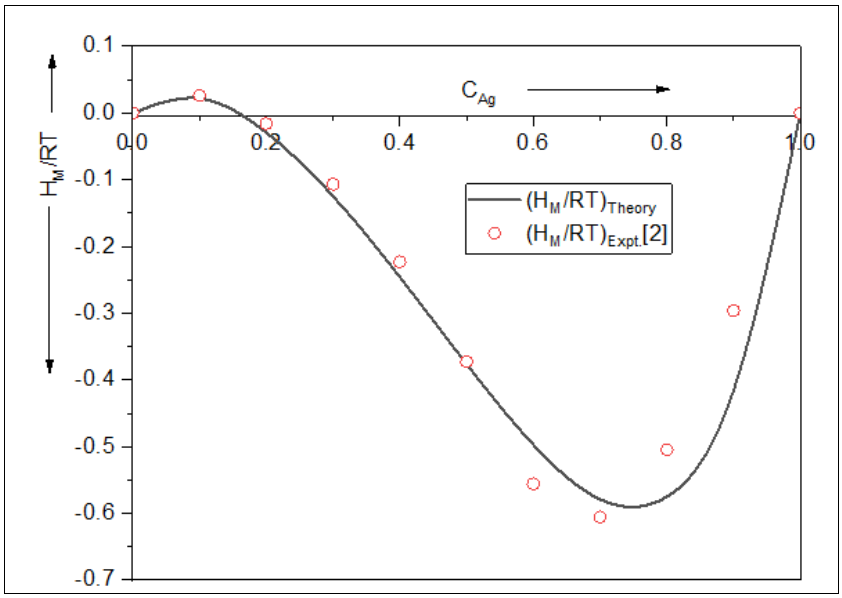

Fig 4: H_M/RT vs C_{Ag} for AgAl melts at 1273 K

Again, equations (7), (8) and (9) are used to determine the theoretical values of $\frac{S_M}{R}$ for AgAl melts at 1273 K. The theoretical data of S_M are compared with experimental data [2] in Fig. 5 which are in well harmony with maxima at C_{Ag} = 0.4 i.e.0.913 (Theory) 0.912 (Experiment). Thus the observed asymmetry in $\frac{S_M}{R}$ are successfully explained by present theoretical model.

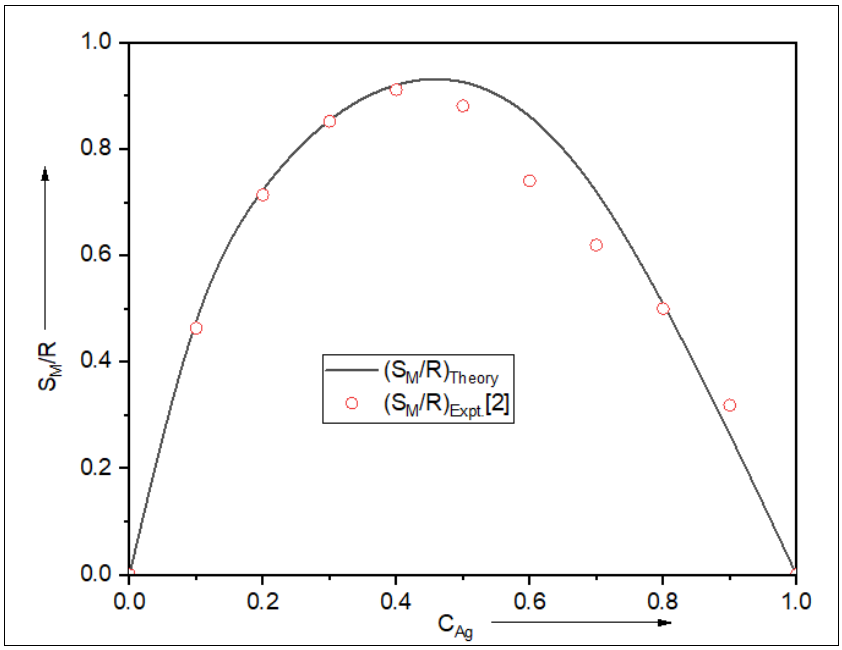

Fig 5: S_M/R vs C_{Ag} for AgAl melts at 1273 K

Now, equation (15) is utilized to compute the concentration dependence of $Scc(0)$ relative to the composition of Ag for AgAl melts at 1273 K. Fig.6 shows the comparison between the theoretical values and experimental values [2] of. $Scc(0)$. There is a reasonable agreement between theory and experiment with minor discrepancies. The theoretical data of $Scc(0)$ indicate maximum value i.e. 0.210 at C_{Ag} = 0.26. Again in the region, 0.11 ≤ C_{Ag} ≤ 0.3, $Scc(0)$ > $Scc^{(id)}(0)$ and $Scc(0) < Scc^{(id)}(0)$ in the region 0.3 ≤ C_{Ag} ≤ 1.0. But the experimental data of $Scc(0) < Scc^{(id)}(0)$ almost in the complete range of concentration i.e. C_{Ag} = 0.1 to 0.9 with maximum value of 0.191 at C_{Ag} = 0.3. However, the results for $Scc(0)$ indicate the ordering behavior of AgAl melts at 1273 K except in the region 0.11 ≤ C_{Ag} ≤ 0.3

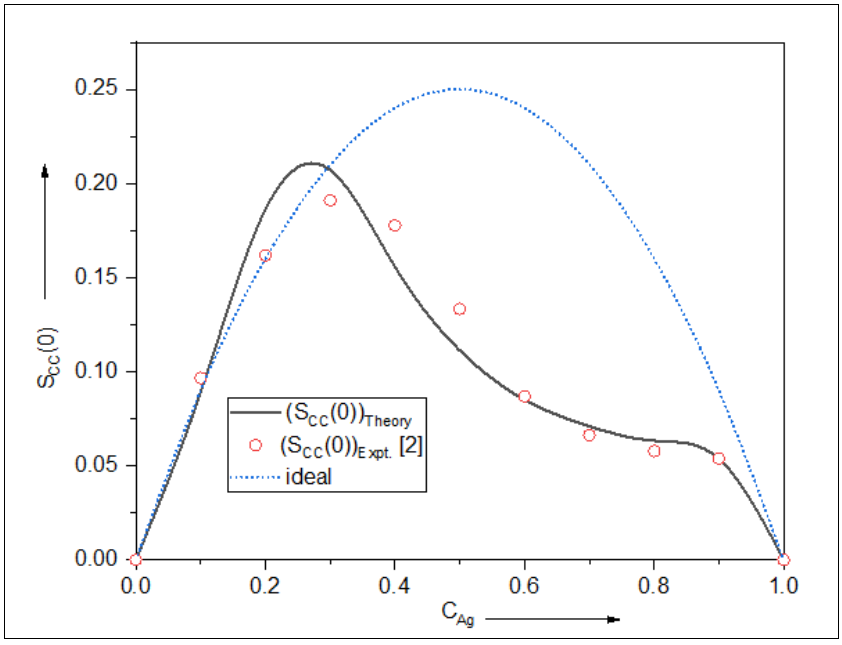

Fig 6: $S_{CC}(0)$ vs C_{Ag} for AgAl melts at 1273 K

The theoretical values of α_1 calculated from equation (18) as a function of concentration of Ag are illustrated in Fig.7. The α_1 - C isotherm exhibits the negative value of α_1 almost each concentration of Ag except in the region $0.11 \leq C_{Ag} \leq 0.3$. Thus, AgAl melts at 1273K is almost ordering in nature.

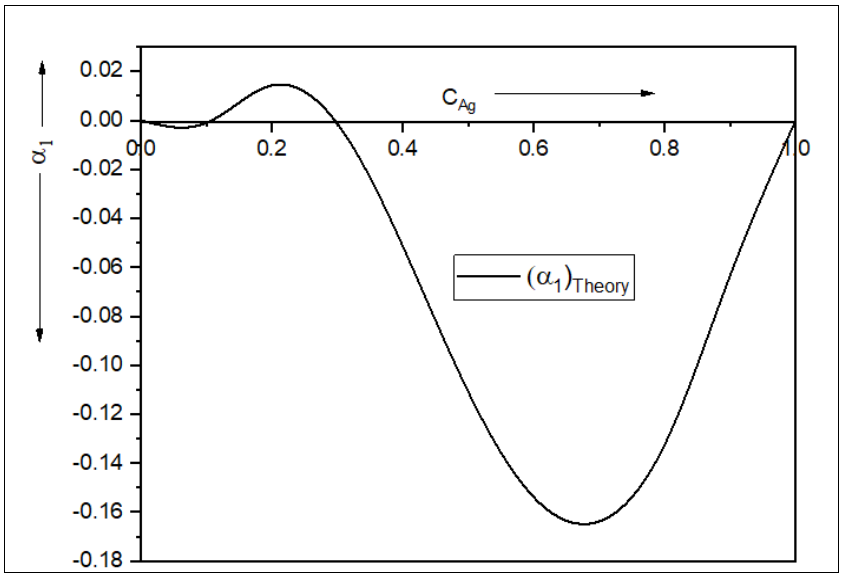

Fig 7: α_1 vs C_{Ag} for AgAl melts at 1273 K

4. Conclusion

The present theoretical analysis successfully describes the observed asymmetries in G_M^{XS}, G_M and S_M of AgAl melts at 1273 K in terms of concentration of Ag. The negative deviations of a_{Ag} and a_{Al} from ideal behavior confirm the ordering nature of AgAl melts at 1273 K. The observed S – shaped nature of $\frac{H_M}{RT}$ is theoretically reproduced. The concentration dependence of $Scc(0)$ and α_1 also indicate that AgAl systems at 1273 K is an ordered alloy.

Therefore, the four-parameter model is suitable model to explain the nature of compound forming liquid alloys.

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