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Thermodynamics of liquid Mg–Sn alloys

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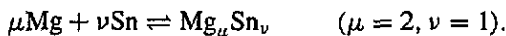
Received 4 August 1992, in final form 11 December 1992

Abstract. The large deviation from the ideal mixture behaviour and the concentration-dependent asymmetry in the thermodynamic properties of Mg–Sn liquid alloys is investigated within a simple theoretical model of heterocoordination (i.e. a model in which there is a preference for unlike atoms to be paired as nearest neighbours). This has been utilized to extract additional microscopic information such as concentration fluctuations and the chemical short-range order parameter. The analysis suggests that heterocoordination leading to the formation of chemical complexes Mg_2Sn is likely to exist in the melt but is only of a weakly interacting nature. The interaction energies between the species of the melt are found to depend considerably on temperature and the alloy is chemically more ordered towards the Mg-rich end of the phase diagram.

1. Introduction

It has been of considerable interest to theoreticians to explain the concentration-dependent asymmetry of the properties of mixing of binary liquid alloys and hence to extract additional microscopic information. Such an asymmetry is usually attributed [1, 2] to the size effect, to the interactions between solute and solvent atoms, or to both. Various properties of Mg–Sn liquid alloys show anomalous behaviour as functions of concentration. The liquidus line [3] (figure 1) is endowed with two eutectics in the terminal regions of the concentration with a bump around the stoichiometric composition Mg_2Sn . The large value of the viscosity [4] and the analysis of the radial distribution function [5] indicate that unlike atoms attract, with the interaction being greatest at the composition Mg_2Sn . The thermodynamic data [3, 6] (see sections 2 and 3) also reveal anomalous behaviour (e.g. the free energy of mixing is a minimum around $C_{Mg} = 0.62$ and the heat of formation is a minimum around $C_{Mg} = 0.66$) in the vicinity of the composition Mg_2Sn .

The size effect ($\Omega_{Sn}/\Omega_{Mg} = 1.112$, where Ω is atomic volume) in the Mg–Sn system is too small to exhibit the observed asymmetries; it is therefore expected that the concentration-dependent asymmetry arises because of energy effects. Since Mg_2Sn is a well defined solid intermediate phase which melts at 1043.7 K, it is likely that such associates, in some form, also exist in the liquid phase. Hereafter, we presume that the number μ of Mg atoms and the number ν of Sn atoms are energetically favoured to form chemical complexes:



Accordingly, the melt of Mg–Sn alloys can be assumed to consist of a mixture of left-over Mg atoms, Sn atoms and a number of chemical complexes Mg_2Sn , all of which are in

chemical equilibrium with each other. The model of complex formation [7, 8] has been used extensively to explain the asymmetry [9–13] of the properties of mixing of a variety of other binary liquid alloys.

In this paper the calculated results of activity, free energy of mixing, heat of formation, entropy of mixing and concentration fluctuations in the long-wavelength limit for Mg–Sn liquid alloys are presented. Section 2 deals with the formalism of free energy of mixing and activity under the complex formation model. The results for heat of formation and entropy of mixing are presented in section 3. In section 4, the results of concentration fluctuations at the long-wavelength limit and hence the stability of the liquid alloys are discussed. The values of chemical short-range order parameters are also given.

2. General formalism, free energy of mixing and activity

A binary alloy contains in all $N_A (= C_A N)$ atoms of A (\equiv Mg) and $N_B (= C_B N)$ atoms of B (\equiv Sn) subject to $C_A + C_B = 1$; $C_A = C$ and $C_B = 1 - C$ are the atomic concentrations, and N is Avogadro's number (for descriptions of the symbols used, see table 1). Following the complex formation model, it is assumed that the chemical complexes Mg_2Sn exist in the molten phase. The binary alloy then consists of n_1 atoms of Mg, n_2 atoms of Sn and n_3 complexes Mg_2Sn . From the conservation of atoms and by setting $N = 1$, one can write

$$\begin{aligned} n_1 &= C - 2n_3 \\ n_2 &= 1 - C - n_3 \\ n &= n_1 + n_2 + n_3 = 1 - 2n_3. \end{aligned} \tag{1}$$

Table 1. The symbols used.

n_1, n_2, n_3	Numbers of Mg atoms, of Sn atoms and of chemical complexes Mg_2Sn respectively in the molten alloy
N	Avogadro's number
C	Concentration
g	Formation energy of the complex Mg_2Sn
V_{ij}	Interaction energies
$\ln a$	Logarithm of the thermodynamic activity
G_M	Free energy of mixing
H_M	Heat of mixing
S_M	Entropy of mixing
$S_{CC}(0)$	Concentration fluctuations, i.e. concentration–concentration correlation function in the long-wavelength limit
α_1	Chemical short-range order parameter

The free energy G_M of mixing of the binary alloy can be expressed as

$$G_M = -n_3g + \Delta G \tag{2}$$

where g is the formation energy of the complex and thus the first term $-n_3g$ represents the lowering of the free energy due to the formation of complexes in the alloy. ΔG represents the free energy of mixing of the ternary mixture of fixed n_1 , n_2 and n_3 whose constituents

Mg, Sn and Mg₂Sn are assumed to interact weakly with one another. The strong bonding between Mg and Sn atoms is taken into account via the formation of the chemical complexes. Using ΔG from the work of Bhatia and Singh [13], the free energy of mixing is given by

$$G_M = -n_3g + RT(n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln n_3) + \sum_{i < j} n_i n_j V_{ij} \quad (3)$$

where R is the gas constant. V_{ij} ($i, j = 1, 2, 3$) are the interaction energies through which the left-over Mg atoms, Sn atoms and Mg₂Sn interact with one other. By definition, V_{ij} are independent of the concentration but may depend on the temperature and pressure. The equilibrium values of n_3 can be obtained via the condition

$$(\partial G_M / \partial n_3)_{T,P,C} = 0. \quad (4)$$

Using equations (3) and (4), we obtain

$$n_1^2 n_2 = 0.406 n_3 K \exp Y \quad (5)$$

where

$$K = \exp(-g/RT) \quad (6)$$

and

$$Y = (n_1 - 2n_3)V_{13}/RT + (n_2 - n_3)V_{23}/RT - (2n_2 + n_1)V_{12}/RT. \quad (7)$$

Equation (5) provides numerically the equilibrium values of n_3 which can be used in equation (3) to obtain the free energy G_M of mixing. It is obvious from equation (3) or (5) that to compute n_3 or G_M we must have knowledge of g and V_{ij} . The interaction energies V_{ij} and g are determined following the method suggested by Bhatia and Hargrove [7]. Since $G_M^{\text{min}} \simeq -2.31RT$, this implies a smaller value for g ; therefore as a starting point we took $g \simeq -(\mu + \nu)G_M$ and then the interaction energies V_{12} , V_{13} and V_{23} are adjusted to yield the concentration dependence of G_M via equations (5) and (3). The process is repeated for different sets of energy parameters until a good fit for G_M is obtained. It may, however, be noted that, once the energy parameters are selected, these remain the same for all other investigations such as activity, concentration fluctuations, heat of mixing and entropy of mixing. The energy parameters g and V_{ij} evaluated for MgSn are

$$g/RT = 5.298 \quad V_{12}/RT = -4.10 \quad V_{13}/RT = -2.50 \quad V_{23}/RT = -5.0. \quad (8)$$

Of the energy parameters, g/RT has a meaningful physical significance because it concerns the formation of the complex in the alloys. It is obvious that g/RT is comparatively smaller in magnitude than for strongly interacting systems [7-11], such as Mg-Bi, Tl-Te, Hg-K and Hg-Na, for which the g/RT -values are 16.7, 10.84, 9.965 and 8.29, respectively. Similarly the evaluated values of the interaction energies (i.e. V_{12} , V_{13} and V_{23}) suggest that the species, i.e. Mg atoms, Sn atoms and the complexes Mg₂Sn of the Mg-Sn liquid alloys, are attractive in nature. In the light of the complex formation energy, MgSn obviously is a weakly interacting system [7] such as Ag-Al and Cu-Sn.

With the energy parameters in equation (8), the equilibrium equation (5) is solved numerically to obtain the values of the number n_3 of chemical complexes and hence the

values of n_1 and n_2 by using equation (1). The values of n_1 , n_2 and n_3 are plotted in figure 2 as functions of Mg concentration; n_3 is a maximum near the stoichiometric composition, i.e. $C_{Mg} = 0.66$. The theoretical and observed [3] values of G_M/RT as functions of concentration are given in table 2 for comparison. Theoretical calculation, using equations (5) and (8) in equation (3), suggests that the minimum in G_M occurs around $C_{Mg} = 0.62$, i.e. $G_M/RT = -2.2706$. Although Hultgren's data provide values of G_M only at gross concentrations, the asymmetry in the computed values of G_M is in accordance with the observed data. The free energy of mixing also suggests that Mg-Sn ($G_M^{\min} = -2.3164RT$) is not as strongly an interacting system as Mg-Bi ($G_M^{\min} = -3.3756RT$) and liquid amalgams, such as Hg-K ($G_M^{\min} = -3.3464RT$) and Hg-Na ($G_M^{\min} = -3.1278RT$).

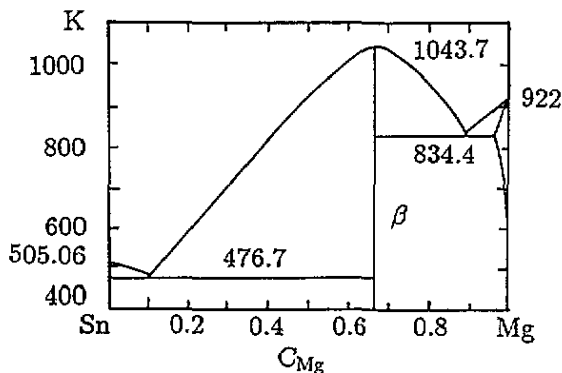


Figure 1. Phase diagram of Mg-Sn alloy [3].

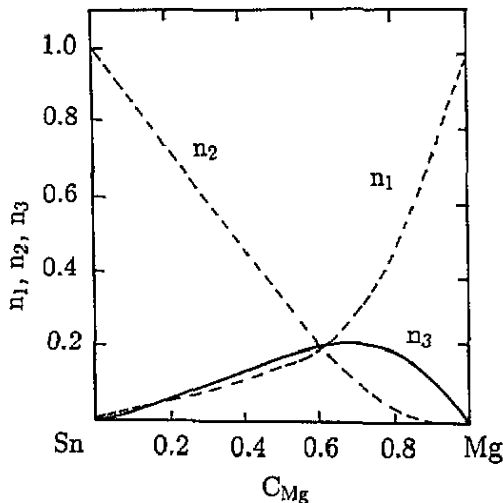


Figure 2. Concentration dependences of n_1 , n_2 and n_3 for Mg-Sn liquid alloys at 1073 K.

Table 2. Free energy G_M/RT of mixing and activity $\ln a_{Mg}$ of Mg-Sn liquid alloys at 1073 K.

C_{Mg}	G_M/RT		$\ln a_{Mg}$	
	Calculated	Observed [3]	Calculated	Observed [3]
0.1	-0.757	-0.725	-6.518	-6.266
0.2	-1.324	-1.285	-5.315	-5.360
0.3	-1.759	-1.741	-4.352	-4.537
0.4	-2.065	-2.080	-3.516	-3.725
0.5	-2.239	-2.281	-2.765	-2.896
0.6	-2.269	-2.316	-2.071	-2.087
0.7	-2.127	-2.154	-1.396	-1.335
0.8	-1.756	-1.758	-0.729	-0.701
0.9	-1.078	-1.079	-0.227	-0.235

The free energy of mixing (equation (3)) can be used to obtain an expression for the activity a_{Mg} of the atom Mg as follows:

$$RT \ln a_A = (\partial G_M / \partial N_A)_{T,P,N_B} = G_M + (1 - C)(\partial G_M / \partial C)_{T,P,N} \quad (A \equiv Mg, B \equiv Sn). \quad (9)$$

With G_M given by equation (3), equation (9) gives, on using equations (1) and (4),

$$\ln a_A = 1 - n + \ln \left(\frac{n_1}{n_2} \right) + \ln n + n_3 \frac{V_{13}}{RT} + n_2 \frac{V_{12}}{RT} - \sum_{i < j} n_i n_j \frac{V_{ij}}{RT}. \quad (10)$$

With the same values of n_i ($i = 1, 2, 3$) and the energy parameters as discussed above, equation (10) has been used to compute $\ln a_{Mg}$ as a function of concentration. The computed values are given in table 2 together with the experimental observations [3]. The theory and experiment are in reasonable agreement.

3. Heat of formation and entropy of mixing

In the complex formation model the evaluation of the heat H_M of formation and the entropy S_M of mixing is of considerable significance because it is likely to show the temperature dependence of the energy parameters g and V_{ij} .

The heat H_M of formation can be obtained using equation (3) and the relation

$$H_M = G_M - T(\partial G_M / \partial T)_{P,C,N}. \quad (11)$$

Equations (3) and (11) provide

$$H_M = -n_3 \left(g - T \frac{\partial g}{\partial T} \right) + \sum_{i < j} n_i n_j \left(V_{ij} - T \frac{\partial V_{ij}}{\partial T} \right) \quad (12)$$

and hence the entropy of mixing

$$S_M = (H_M - G_M) / T. \quad (13)$$

One readily infers from equation (12) that, if the energy parameters are independent of temperature ($\partial g/\partial T = \partial V_{ij}/\partial T = 0$), then the heat of formation simply becomes

$$H_M = -n_3g + \sum_{i < j} n_i n_j V_{ij}. \quad (14)$$

In such a situation, H_M can be evaluated from knowledge of n_i , g and V_{ij} as determined earlier. We have observed that H_M and similarly S_M so obtained are in very poor agreement with the experimental observations. This simply suggests the importance of the dependence of the energy parameters on temperature. We have used equation (12) to ascertain the variation in energy parameters with temperature from the observed [14] values of H_M . The results are

$$\begin{aligned} \partial g/\partial T &= -0.6615R & \partial V_{12}/\partial T &= 0 & \partial V_{13}/\partial T &= -0.842R \\ \partial V_{23}/\partial T &= -0.962R \end{aligned} \quad (15)$$

i.e. all the energy parameters, except V_{12} , have negative temperature coefficients. V_{12} , which signifies the interaction of left-over Mg and Sn atoms in the alloy, does not exhibit temperature variation.

The computed results for H_M and S_M^{xs} ($= S_M + R \sum_{i=1}^2 C_i \ln C_i$) are given in table 3 and are compared with the other theoretical [15] and experimental [14] observations. The theoretical results of Lele and Ramachandra Rao [15] were obtained using the regular associated-solution model in which the existence of Mg_2Sn complexes is assumed. It is evident that the heat of formation is negative at all concentrations, being a minimum around the stoichiometric Mg concentration $C_{Mg} = 0.66$. It is interesting to observe that the concentration-dependent asymmetry in H_M as observed from experiment can be explained if one considers the temperature dependence of the energy parameters for Mg-Sn liquid alloys.

Table 3. Computed and observed values of the heat H_M/RT of formation and excess entropy S_M^{xs} of mixing of Mg-Sn liquid alloys.

C_{Mg}	H_M/RT			S_M^{xs}/R		
	Theory		Observed [14]	Theory		
	Present	[15] ^a		Present	[15] ^a	Observed [14]
0.1	-0.428	-0.414	-0.371	0.031	-0.105	0.242
0.2	-0.804	-0.808	-0.741	0.164	-0.017	0.366
0.3	-1.114	-1.149	-1.083	0.281	-0.152	0.390
0.4	-1.353	-1.413	-1.369	0.321	-0.050	0.312
0.5	-1.515	-1.576	-1.557	0.258	0.097	0.253
0.6	-1.585	-1.615	-1.623	0.091	0.229	0.171
0.7	-1.523	-1.513	-1.528	-0.058	0.245	0.121
0.8	-1.243	-1.254	-1.247	0.103	0.056	0.082
0.9	-0.701	-0.762	-0.750	0.436	-0.086	0.028

^a Lele and Ramachandra Rao.

Further, the computed values of excess entropy of mixing from the present study yield a negative value at $C_{Mg} = 0.7$ which is close to stoichiometric Mg concentration $C_{Mg} = 0.66$. The positive values of S_M^{xs} at all other concentrations indicate that Mg-Sn is more ordered

around the stoichiometric Mg concentration than at other concentrations. The experimental observations, however, do not indicate the negative value of S_M^{XS} at the said concentration. At other concentrations, however, our values are in better agreement with the experimental observation than those obtained by Lele and Ramachandra Rao [15].

4. Concentration fluctuations at long-wavelength limit and chemical short-range order parameter

Since the inception of the number-density structure factors [16] $S_{CC}(q)$, $S_{NN}(q)$ and $S_{NC}(q)$, the long-wavelength limit of the concentration fluctuations has been widely used [2, 17, 18] to study the nature of atomic order in binary liquid alloys. The basic advantage is that $S_{CC}(0)$ can be determined by making use of the thermodynamic relations

$$S_{CC}(0) = RT(\partial^2 G_M / \partial C^2)_{T,P,N}^{-1} = (1 - C)a_A(\partial a_A / \partial C)_{T,P,N}^{-1} = C a_B [\partial a_B / \partial (1 - C)]_{T,P,N}^{-1} \tag{16}$$

The last two equalities of equation (16) can be directly used to obtain $S_{CC}(0)$ from the observed activity data. Such $S_{CC}(0)$ are usually termed experimental values. As regards the theoretical expressions, equations (3) and (16) can be used to express $S_{CC}(0)$:

$$S_{CC}^{-1}(0) = \sum_{i=1}^3 \frac{(n'_i)^2}{n_i} + 2 \sum_{i < j} n'_i n'_j \frac{V_{ij}}{RT} \tag{17}$$

where a prime denotes differentiation with respect to C , i.e.

$$n'_1 = 1 - 2n'_3 \tag{18}$$

$$n'_2 = -1 - n'_3 \tag{19}$$

where n'_3 can be obtained by differentiating equation (5):

$$n'_3 = (2/n_1 - 1/n_2 - V_{13}/RT + V_{23}/RT - V_{12}/RT) \div (4/n_1 - 1/n_2 + 1/n_3 - 4V_{13}/RT - 2V_{23}/RT + 4V_{12}/RT). \tag{20}$$

The computed values of $S_{CC}(0)$ from equation (17) and those from activity data [3] are plotted in figure 3. $S_{CC}(0)$ -values computed from the complex formation model are in reasonable agreement with those obtained directly from activity data. It may also be mentioned that McAlister *et al* [19] have also computed $S_{CC}(0)$ from the activity data of Eldridge *et al* [20] and found a weak minimum around the concentration Mg_2Sn . Hultgren *et al* [3], on the other hand, judiciously selected the data for Mg-Sn from various experimental measurements including those of Eldridge *et al* [20] which have been used in the present study. The latter data do not show any minimum around the said concentration, as is evident from figure 3.

Recently Singh and co-workers [2, 21, 22] have used the variation in $S_{CC}(0)$ with concentration to understand the nature of atomic order in binary liquid alloys. It may be recalled that the deviation of $S_{CC}(0)$ from the ideal values ($S_{CC}^{id}(0) = C_A C_B$) can be used to visualize the nature of atomic order in the alloys. If, at a given composition,

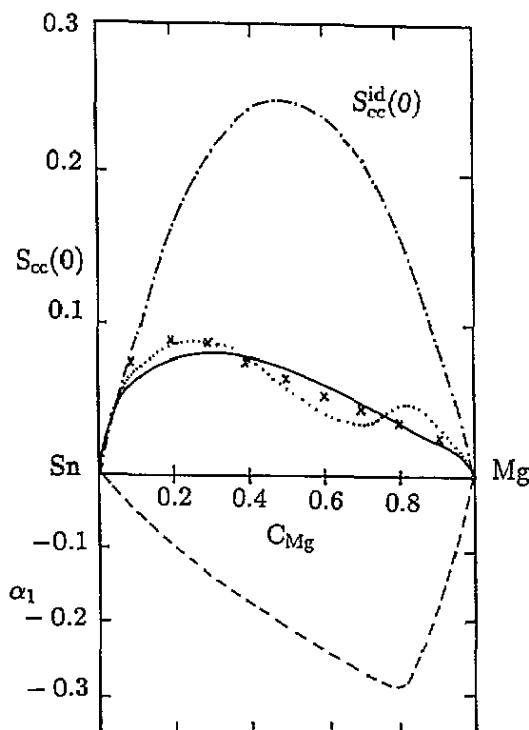


Figure 3. Concentration fluctuations $S_{CC}(0)$ and short-range order parameters α_1 of Mg-Sn liquid alloys at 1073 K: —, theory; x, computed directly from activity; ·····, results obtained by McAlister *et al* [19]; - · - ·, ideal values for $S_{CC}(0)$; — — —, theoretical value of α_1 .

$S_{CC}(0) - S_{CC}^{id}(0)$ is positive, then there is a tendency for segregation and, if $S_{CC}(0) - S_{CC}^{id}(0)$ is negative, ordering in the alloy is expected.

Figure 3 indicates that $S_{CC}(0)$ for Mg-Sn is smaller than $S_{CC}^{id}(0)$ at every concentration and is quite asymmetric around the equiatomic composition. That is to say that order (preference for unlike atoms to be paired as nearest neighbours) exists in the molten alloys of the Mg-Sn system. The maximum deviation from ideal behaviour occurs at $C_{Mg} = 0.66$. However, $S_{CC}(0)$ for Mg-Sn does not exhibit any distinctive minimum around the stoichiometric composition as has been observed for other strongly interacting systems [7, 23] such as Mg-Bi and Li-Pb.

In order to quantify the degree of order, the Warren-Cowley [24, 25] short-range order parameter α_1 for Mg-Sn liquid alloys has been computed. Experimentally α_1 can be determined from the concentration-concentration structure factors $S_{CC}(q)$ and the number-number structure factors $S_{NN}(q)$. However, it is difficult in practice to determine $S_{CC}(q)$ and $S_{NN}(q)$ for all kinds of binary liquid alloy [17, 18, 26, 27]. On the other hand, α_1 can be evaluated theoretically from knowledge of $S_{CC}(0)$ [2, 13]. α_1 provides immediate insight into the local arrangements of the atoms in the mixture. $\alpha_1 = 0$ corresponds to a random distribution, $\alpha_1 < 0$ refers to unlike atoms pairing as nearest neighbours whereas $\alpha_1 > 0$ corresponds to like atoms pairing in the first coordination shell. From a simple probabilistic approach, one can easily show that the limiting values of α_1 lie in the range

$$-C/(1-C) \leq \alpha_1 \leq 1 \quad C \leq \frac{1}{2} \quad (21)$$

$$-(1-C)/C \leq \alpha_1 \leq 1 \quad C \geq \frac{1}{2} \quad (22)$$

For equiatomic composition the above relations simply reduce to

$$-1 \leq \alpha_1 \leq +1. \quad (23)$$

The minimum possible value $\alpha_1^{\min} = -1$ means complete order of unlike atoms as nearest neighbours, whereas the maximum value $\alpha_1^{\max} = 1$ suggests that like-atom pairs in the alloy are totally segregated. Recently Singh *et al* [28] have suggested that α_1 also can be computed from $S_{CC}(0)$:

$$\alpha_1 = (S - 1)/[S(Z - 1) + 1] \quad S = S_{CC}(0)/S_{CC}^{\text{id}}(0) \quad (24)$$

where Z is the coordination number. For the present purpose, Z is taken as 10 and the $S_{CC}(0)$ -values are as evaluated above. The computed values of α_1 as a function of concentration are also plotted in figure 3. The minimum of α_1 ($\alpha_1 = -0.29$) occurs at $C_{\text{Mg}} = 0.8$. The asymmetry in α_1 is distinctly visible. Further we observe that the Mg-rich end of the phase diagram is more ordered than the Sn-rich end.

5. Conclusions

(i) The thermodynamic functions computed for Mg-Sn liquid alloys exhibit marked deviation from the ideal mixture behaviour.

(ii) The concentration-dependent asymmetries can be successfully produced by considering the existence of heterocoordinated complexes Mg_2Sn in the liquid phase.

(iii) The concentration fluctuations are found to be lower than the ideal values at every concentration, being lowest around Mg_2Sn , but do not exhibit a distinctive minimum around the stoichiometric composition. It has been assumed that the formation of the complexes Mg_2Sn is of a weak nature in the liquid phase. Heterocoordination persists at all concentrations but the Mg-rich end of the phase diagram is more ordered.

(iv) The energy parameters of Mg-Sn liquid alloys are strongly temperature dependent.

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