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Small-angle structure and atomic order in Ge- and Si-based liquid alloys

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Abstract. The chemical and topological order of AgSi, AgGe and AlGe liquid alloys are investigated from the thermodynamic equations. On mixing, the component elements (Si, Ge, Al and Ag) undergo noticeable structural change. This suggests that AgSi is a segregating system, AlGe is chemically more ordered and AgGe undergoes inversion from order to segregation as a function of concentration.

Si and Ge, which are semiconductors in the solid phase, undergo large volume contraction on melting and thereby lose distinguished structural features to conform to a common liquid metal pattern. Furthermore, the change in entropy and the excess entropy at melting suggest that compared to the average metals, say Ag and Al, Si and Ge are less ordered in the liquid phase, and so it is of interest to make a structural analysis of the alloys of Si and Ge in the molten state.

Of the Si and Ge alloys AgSi, AgGe and AlGe concern us most, as these are simple eutectic systems with extremely small solid solubilities. The liquidus lines [1] (melting temperature versus concentration) are sketched in figure 1, and exhibit a deep eutectic occurring in AlGe followed by AgGe and AgSi towards the terminal region of Al- or Ag-rich concentrations. Although the small values of the size effect ($\Omega_{Ge}/\Omega_{Al} = 1.16$, $\Omega_{Ag}/\Omega_{Si} = 1.04$ and $\Omega_{Ge}/\Omega_{Ag} = 1.11$, Ω being the atomic volume) and the electronegativity difference ($X_{Ge} - X_{Al} = 0.3$, $X_{Ag} - X_{Si} = 0.1$ and $X_{Ag} - X_{Ge} = 0.1$, X being the electronegativity) of the constituent elements make them suitable for forming good solid solutions, as per Hume-Rothery empirical requirements, this is not accomplished. As regards the excess free energy of mixing [1] (G_{XS}), AlGe liquid alloys are endothermic, AgSi alloys are exothermic and AgGe alloys undergo inversion from endothermic (Ag-rich end) to exothermic (Ge-rich end).

It is likely that the chemical short-range order and the topological short-range order of these systems depend strongly on concentration and are responsible for the characteristic behaviour. The coordination number [2] of Al and Ag near the melting point ($Z_{Al} = 11.5$ and $Z_{Ag} = 11.3$) are quite different from those of pure Si and Ge ($Z_{Si} = 6.4$ and $Z_{Ge} = 6.8$) and therefore change from a close-packed to more open structure is expected during the mixing. With this in mind, we propose to investigate the small-angle partial structure factors [3], namely the concentration fluctuations, $S_{cc}(0)$, density fluctuations, $S_{NN}(0)$, and the coupling term, $S_{Nc}(0)$, from the thermodynamic data. These

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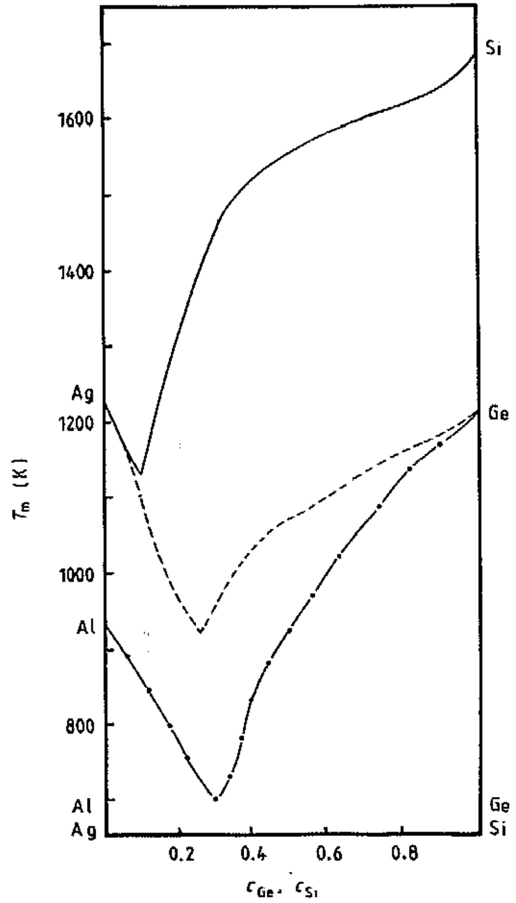

Figure 1. Liquidus lines: ———, AgSi; – – –, AgGe; –·–·–, AlGe.

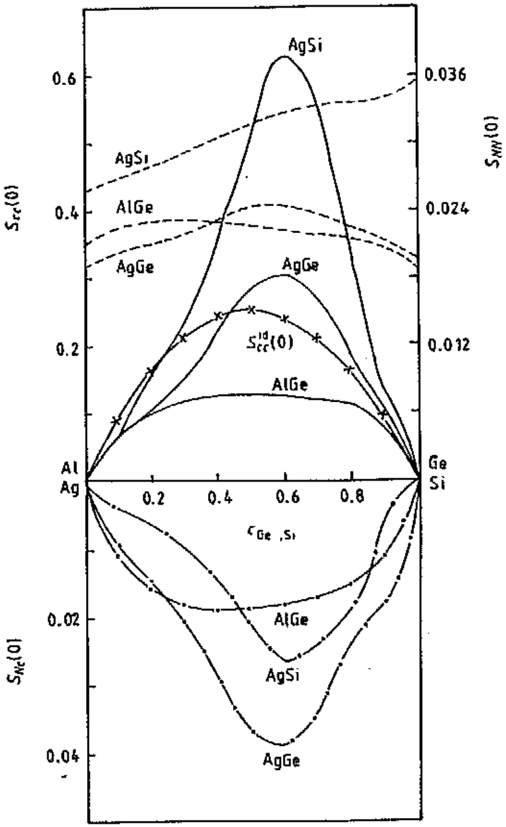

Figure 2. Number–concentration structure factors at the long-wavelength limit for AgSi (1700 K), AgGe (1250 K) and AlGe (1200 K) liquid alloys: ———, $S_{cc}(0)$; –×–×–, $S_{cc}^{id}(0)$; – – –, $S_{NN}(0)$; –·–·–, $S_{Nc}(0)$.

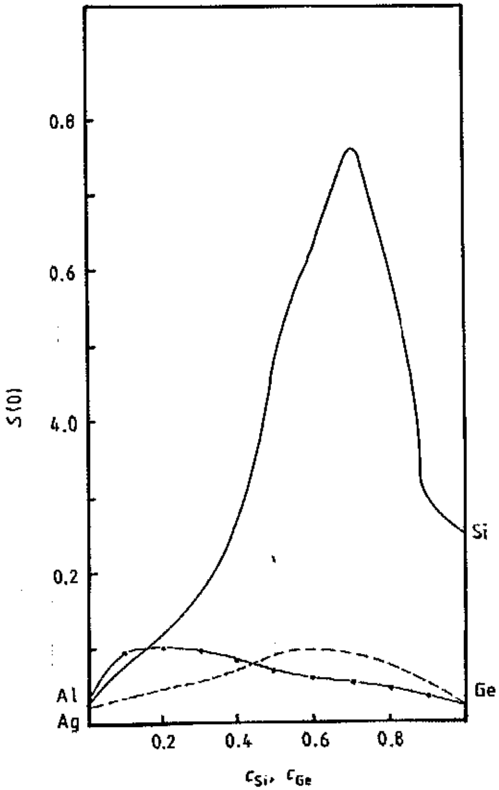

Figure 3. Total structure factors, $S(0)$, at the long-wavelength limit: ———, AgSi; – – –, AgGe; –·–·–, AlGe.

factors are of immense help [4–6] in shedding light on the nature of atomic order in liquid alloys. For example, the $S_{cc}(0)$ are useful for visualizing the nature of chemical order whereas the $S_{NN}(0)$ can be used to interpret the topological order. As these fluctuations cannot be determined successfully [7] from diffraction experiment, a theoretical investigation like this is needed.

Bhatia and Thornton [3] showed that the total scattered intensity, $I(q)$, can be expressed as

$$I(q) = (\bar{b})^2 S_{NN}(q) + (\Delta b)^2 S_{cc}(q) + 2\bar{b}(\Delta b) S_{Nc}(q) \tag{1}$$

where $\bar{b} = c_A b_A + c_B b_B$, $\Delta b = b_A - b_B$. b_i and c_i represent atomic scattering factors and the concentration of the component i respectively. $S_{cc}(q)$, $S_{NN}(q)$ and $S_{Nc}(q)$ are the number concentration structure factors that are associated with concentration–concentration, density–density and density–concentration correlations respectively. In the long-wavelength limit ($q \to 0$), equation (1) can be expressed as

$$I(0) = S(0)\overline{b^2} = (\bar{b})^2 S_{NN}(0) + (\Delta b)^2 S_{cc}(0) + 2\bar{b}(\Delta b) S_{Nc}(0) \tag{2}$$

where $\overline{b^2} = c_A b_A^2 + c_B b_B^2$ and $S(0)$ is the long-wavelength limit of the total structure factor. $S_{cc}(0)$, $S_{NN}(0)$ and $S_{Nc}(0)$ have useful physical meanings for binary liquid alloys:

$$S_{cc}(0) = N\langle(\Delta c)^2\rangle \tag{3}$$

$$S_{NN}(0) = \langle(\Delta N)^2\rangle/N \tag{4}$$

$$S_{Nc}(0) = \langle\Delta N\,\Delta c\rangle \tag{5}$$

where $\langle(\Delta c)^2\rangle$ is the mean square fluctuation in concentration, $\langle(\Delta N)^2\rangle$ is the mean square fluctuation in the number of particles and $\langle\Delta N\,\Delta c\rangle$ is the correlation between the two fluctuations. To express these fluctuations [3] in terms of thermodynamic functions, one writes

$$S_{cc}(0) = c_B a_A (\partial a_A/\partial c_A)^{-1}_{T,P,N} = c_A a_B (\partial a_B/\partial c_B)^{-1}_{T,P,N} \tag{6}$$

$$S_{NN}(0) = \rho k_B T \chi_T + \theta^2 S_{cc}(0) \tag{7}$$

$$S_{Nc}(0) = -\theta S_{cc}(0) \tag{8}$$

$$\theta = (1/V)(\partial V/\partial c)_{T,P,N} \tag{9}$$

where a_A and a_B are activities of the component elements, V is the molar volume, ρ is the number density and χ_T stands for isothermal compressibility. θ is the dilatation factor. The basic function in the above relations is the concentration fluctuation, $S_{cc}(0)$, which can be evaluated from the observed activity. For this purpose we have taken activity data for AlGe at 1200 K, AgGe at 1250 K and AgSi at 1700 K, as compiled by Hultgren *et al* [1]. With a view to minimizing the uncertainty in the numerical differentiation, we made a power series expansion of the activity–concentration data and then determined $(\partial a_i/\partial c_i)$. The last two terms of equation (6) provide a cross-check on the values of $S_{cc}(0)$. ρ and χ_T needed in the calculation of $S_{NN}(0)$ are taken from the experimental measurements [8–9].

For the alloys we have considered,

$$V = c_A V_A + c_B V_B \qquad \chi_T = c_A \chi_A + c_B \chi_B. \tag{10}$$

The values of $S_{cc}(0)$ and $S_{NN}(0)$ for AlGe, AgGe and AgSi are plotted in figure 2. It

Table 1. The chemical short-range order parameter (α_1) for AgSi, AlGe and AgGe liquid alloys.

c_A; A = Al, Ag	AgSi α_1	AgGe α_1	AlGe α_1
0.1	0.050	0.024	−0.019
0.2	0.077	0.020	−0.054
0.3	0.086	0.027	−0.085
0.4	0.080	0.025	−0.098
0.5	0.062	0.014	−0.095
0.6	0.035	−0.008	−0.084
0.7	0.009	−0.035	−0.068
0.8	−0.004	−0.049	−0.052
0.9	0.002	−0.029	−0.026

indicates that the $S_{cc}(0)$ for AlGe, AgGe and AgSi deviate considerably from the ideal values $S_{cc}^{id}(0)$ ($=c_A c_B$). The maximum deviation occurs in AgSi, followed by AlGe and AgGe. We may recall that the deviation of $S_{cc}(0)$ from ideal values is usually attributed [10, 11] to the size effect or to the strong interactions between the solute and the solvent. Since the size effects in AgSi, AlGe and AgGe are very small it is likely that the deviations in $S_{cc}(0)$ are due to the interatomic potentials of the constituent species.

In the past $S_{cc}(0)$ has been widely used [12, 13] to interpret the nature of chemical order in binary liquid alloys. On the one hand, if, at a given concentration, $S_{cc}(0) \ll S_{cc}^{id}(0)$, then there is a tendency for strong association among unlike atoms leading to the existence of chemical complexes in the mixture; on the other hand, $S_{cc}(0) \gg S_{cc}^{id}(0)$ suggests segregation or phase separation. Although the liquidus curves for these alloys are alike, the natures of the interactions among the constituent species are quite at variance. The values of $S_{cc}(0)$ suggest that AgSi is a segregating system at most of the concentrations, except at a very narrow band around $c_{Si} \simeq 0.2$. The maximum segregation occurs around 60 at.% of Si. However, at $c_{Si} = 0.2$, the computed value of $S_{cc}(0)$ ($=0.155$) is slightly lower than $S_{cc}^{id}(0)$ ($=0.16$). Unlike AgSi, AgGe undergoes inversion of chemical order. For $0.44 > c_{Ge} > 0$, AgGe is more ordered than in the region $1.0 > c_{Ge} > 0.44$. In the latter concentration range, there is a tendency towards segregation, but its degree is quite small compared to that for AgSi. $S_{cc}(0)$ of AlGe is always smaller than $S_{cc}^{id}(0)$, which indicates that unlike-atom pairing occurs at nearest neighbours. Obviously AlGe is chemically more ordered than AgSi and AgGe.

In order to quantify the chemical order, we have also computed Warren–Cowley [14, 15] short-range order parameters. The latter, for the first coordination shell, can readily be obtained from $S_{cc}(0)$ following a simple relation [16]:

$$\alpha_1 = (S-1)/[S(Z-1)+1] \qquad S = S_{cc}(0)/S_{cc}^{id}(0). \tag{11}$$

It may, however, be noted that the equation (11) is the approximate version of an (exact) sum rule [17, 18] relating $S_{cc}(0)$ and α_1, but it can safely be used for the first coordination shell. The coordination number Z has been taken as the concentration average of the values for pure components. The computed values of α_1 are tabulated in table 1. α_1 for AgSi is positive at all concentrations except at 20 at.% of Si where it is negative. The small negative values indicate the weak tendency towards ordering of unlike-atom pairs as nearest neighbours in AgSi at the said concentration. At all other concentrations α_1 suggests segregation. The negative values of α_1 for AlGe at all concentrations suggest order. We recall [19] that $\alpha_1^{\max} = +1$ means complete segregation while $\alpha_1^{\min} = -1$ means perfect order. The magnitudes of the values of α_1, as in table 1, should be viewed as the degrees of order or segregation. It may also be noted that a segregation-to-order transformation, but of weak nature, occurs in AgGe.

Likewise $S_{cc}(0)$ and $S_{NN}(0)$ can be used to interpret the topological order in binary liquid alloys. It is evident that the topological order in AgSi varies almost linearly with concentration from the Ag to the Si end. The natures of topological order in AgGe and AlGe, however, differ from that of AgSi. $S_{Nc}(0)$ values, as plotted in figure 2, further indicate that there is strong coupling between number density and concentration fluctuations in these systems. The coupling between two fluctuations is maximal in AgGe, followed by AgSi and AlGe.

With a view to maintaining internal consistency, the values $S_{cc}(0)$, $S_{NN}(0)$ and $S_{Nc}(0)$ are further used to obtain the compressibility of liquid alloys as a function of concentration. Equations (6) to (9) yield

$$\rho k_{\mathrm{B}} T \chi_T = (S_{NN}(0) S_{cc}(0) - S_{Nc}^2(0)/S_{cc}(0). \tag{12}$$

The χ_T so obtained agree very well with that derived from simple approximations, as in (10). This suggests that the χ_T of these liquid alloys can safely be approximated by the linear relation (10); however, a true knowledge from experiment is desirable.

The values of $S_{NN}(0)$, $S_{cc}(0)$ and $S_{Nc}(0)$ as computed from the thermodynamic data have also been used in equation (2) to obtain the total structure factor $S(0)$ in the long-wavelength limit. The values of the atomic scattering factors, b_i, required in (2) are taken from the work of Hansen *et al* [20]. These are plotted in figure 3. $S(0)$ of AgSi is distinctively different from that for AlGe and AgGe and depends strongly on the concentration. $S(0)$ for AgSi is maximal around $c_{\mathrm{Si}} = 0.7$. Such large values of $S_{cc}(0)$ and $S(0)$ for AgSi can be interpreted as a tendency towards phase separation. Although the values of $S(0)$ for AlGe and AgGe are quite small in comparison to that for AgSi, they differ among themselves as regards the position of the asymmetry. $S(0)$ in AlGe is asymmetric towards the Al-rich end whereas AgGe is asymmetric towards the Ge-rich end.

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