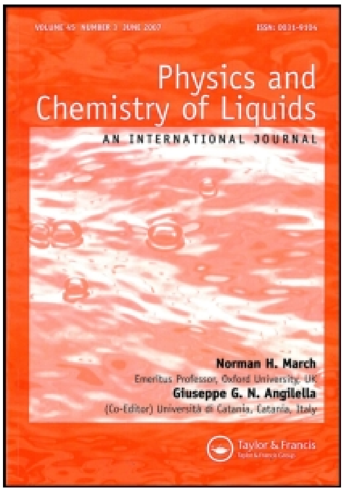

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Temperature Dependent Interchange Energy of the Liquid Alloy $Na_{0.85}Cs_{0.15}$

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Small-angle x-ray diffraction data on the liquid alloy $Na_{0.85}Cs_{0.15}$ at temperatures from 80 to 190 °C are presented. The analysis will be given on the basis of the Flory model, introducing a temperature dependent interchange energy. This concept brings more consistency in the results of diffraction, calorimetric and EMF measurements.

I INTRODUCTION AND THEORY

In this short paper we present the results and analysis of some x-ray diffraction experiments on the liquid sodium-caesium alloy $Na_{0.85}Cs_{0.15}$, carried out as a function of temperature in the range from 80 to 190 °C. Diffraction measurements at 80 and 100 °C on this alloy have already been published (Huijben *et al.*[1]). Our attention will be focussed on the small-angle behaviour of the structure factor $S(\mathbf{q})$. As reported by Huijben *et al.*[1,2] this liquid alloy shows a distinct rise of the intensity at small q-values. Appreciable concentration fluctuations, indicating a tendency to phase separation, occur in the liquid, culminating at a sodium concentration of approximately 0.85.

In the analysis of our results we introduce a temperature dependent interchange energy w into the Flory model,[3] in order to bring more mutual consistency in the theoretical description of the x-ray, enthalpy and EMF measurements on the Na-Cs alloys system. The w is defined as twice the energy increase occurring when, starting from two pure liquids A and B, an interior atom of kind A and an interior atom of kind B are interchanged. We mention that the assumption of a temperature dependent interchange energy (or energies for multicomponent systems) in the regular solution and Flory models has been used previously to obtain a more consistent interpretation of some of the thermodynamic results in a number of liquid alloys.[4–7] The analysis presented here however has not been given before.

As already stated by Huijben *et al.*[1] and Visser *et al.*,[8] three different values for the interchange energy parameter $W(W = w/kT)$ are found for the Na-Cs alloys system, depending on which experiment was taken to be fitted. They obtained $W = 1.04$, 0.77 and 1.14 by fitting to the structure factor at $\mathbf{q} = 0$, the enthalpy of mixing and the EMF data, respectively, over the whole concentration range. The latter value was taken from Bhatia and March.[9]

To analyse the data, we applied the well-known Flory model[3] introduced by Bhatia and March[9] in the theory of liquid alloys. This model must be used rather than the model of regular solutions, when the ratio of the atomic volumes of the two components, γ, is larger than 2. For Na-Cs $\gamma = 3.0$. The Flory formula for the Gibbs free energy of mixing, $\Delta_m G$, is given by

$$\Delta_m G = RT[c \ln \phi + (1 - c) \ln (1 - \phi) + c(1 - \phi)W], \tag{1}$$

where $\phi = c/[c + \gamma(1 - c)]$, the volume fraction of the smaller atoms with atomic concentration c. Equation (1) can be written as

$$\Delta_m G = RT[\alpha(c) + \beta(c)W], \tag{2}$$

with

$$\alpha(c) = c \ln \phi + (1 - c) \ln (1 - \phi) \tag{3}$$

$$\beta(c) = c(1 - \phi). \tag{4}$$

The entropy of mixing, $\Delta_m S$, and the enthalpy of mixing, $\Delta_m H$, are given by the thermodynamic relations:

$$\Delta_m S = -\frac{\partial}{\partial T}(\Delta_m G) \tag{5}$$

and

$$\Delta_m H = \Delta_m G - T\frac{\partial}{\partial T}(\Delta_m G) = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta_m G}{T}\right). \tag{6}$$

Substitution of Eq. (2) into Eqs. (5) and (6) and supposing w being temperature dependent leads to

$$\Delta_m S = -R\alpha(c) - N\beta(c)\frac{\partial w(T)}{\partial T} \tag{7}$$

and

$$\Delta_m H = N\beta(c)\left[w(T) - T\frac{\partial w(T)}{\partial T}\right] = N\beta(c)w', \tag{8}$$

with $w' = w - T\partial w/\partial T$ and $N = R/k$, the Avogadro constant. Here we have assumed that $\alpha(c)$ and $\beta(c)$ are independent on temperature.

If one also introduces a temperature dependence of ϕ(via γ), we obtain the following formula for $\Delta_m H$:

$$\Delta_m H = RT\beta(c)\left[W' + T\frac{1}{\gamma}\frac{\partial\gamma}{\partial T}\left(1 - \frac{1}{\gamma} - \phi W\right)\right], \tag{9}$$

where $W' = w'/kT$. Comparison with Eq. (8) shows that the temperature dependence of γ gives rise to the extra term $(T/\gamma)(\partial\gamma/\partial T)(1 - 1/\gamma - \phi W)$. With $T \simeq 400\ K$, $\gamma = 3$ and using the measured density expansion coefficients of Na and Cs (Huijben *et al.*[10]), we calculate for this term: $0.007\ (1 - W)$. With W and W' being of the order of 1 we can see from Eq. (9) that this term can be neglected in comparison with W'.

Previously, it has been shown that an analysis in terms of the simple Flory model ($\partial w/\partial T = 0$) is adequate for liquid Na-K (Alblas and Van der Lugt[11]) (although the experimental $S_{CC}(0)$ were almost too unreliable to allow an appropriate analysis) and liquid K-Cs (Alblas *et al.*[12]), but not for liquid Na-Cs (Huijben *et al.*[1]). For Na-Cs it will appear that if we use a temperature dependent w, there is more agreement between the interchange energies calculated from the x-ray structural data, the enthalpy measurements[13] and the EMF data.[14]

Bhatia and March[9] showed that within the Flory model we can write the following equation for the small-angle limit of the concentration fluctation structure factor, $S_{CC}(0)$, defined by Bhatia and Thornton[15]:

$$S_{CC}(0) = \frac{c(1-c)}{[1 - c(1-c)f(c)]}, \tag{10}$$

with

$$f(c) = \{2\gamma^2 W - (\gamma - 1)^2[\gamma - c(\gamma - 1)]\}[\gamma - c(\gamma - 1)]^{-3}. \tag{11}$$

From the measured small-angle structure factor $S(0)$, $S_{CC}(0)$ can be deduced by the thermostatistic formula (Huijben *et al.*[2])

$$S(0) = \frac{\langle f\rangle^2}{\langle f^2\rangle}\left[\left(\delta - \frac{f_1 - f_2}{\langle f\rangle}\right)^2 S_{CC}(0) + \rho_0 kT\chi_T\right], \tag{12}$$

where $\langle f \rangle = c_1 f_1 + c_2 f_2$, $\langle f^2 \rangle = c_1 f_1^2 + c_2 f_2^2$, δ is the dilatation factor ($\delta = (1/V)(dV/dc)_N$), ρ_0 the atomic number density and χ_T the isothermal compressibility. Furthermore, c_1 is the atomic fraction and f_1 the atomic scattering factor at $\mathbf{q} = 0$; the index 1 refers to sodium. Finally, for $S_{CC}(0)$ we have the thermodynamic relation (Krishnan and Bhatia,[16] Bhatia and Thornton[15]):

$$S_{CC}(0) = N < (\Delta c_1)^2 > = NkT\left(\frac{\partial^2 G}{\partial c_1^2}\right)^{-1}_{p,T,N} = c_2\left(\frac{\partial \ln a_1}{\partial c_1}\right)^{-1}_{T,N}, \quad (13)$$

where N is the total number of atoms and a_i is the chemical activity of component i.

II EXPERIMENTS, RESULTS, DISCUSSION

For the experimental arrangement we refer to Huijben and Van der Lugt.[17] The procedures for carrying out the small-angle measurements have been discussed by Huijben *et al.*[1,2] The wavevector $\mathbf{q}$ in the small-angle experiment covered a range from 0.12 to 0.75 Å^{-1}. Intensities below 0.12 Å^{-1} have to be obtained by extrapolation because of the presence of a strong central beam. For the extrapolation procedure and a discussion of the agreement between small- and larger-angle results we refer to Alblas and Van der Lugt[11] and Huijben *et al.*[2] The corrections applied to the raw x-ray data are described extensively in Huijben and Van der Lugt.[17] For three of the applied temperatures, the larger-angle results were available from Huijben *et al.*[1] For other temperatures for which small-angle measurements have been carried out in this paper we used inter- or extrapolations of $S(\mathbf{q})$ with respect to the measurements of Huijben *et al.*[1] This procedure is justified because in the region of overlap, the temperature dependence of the latter is relatively small.

The measurements have been carried out on one sample of $Na_{0.85}Cs_{0.15}$ ($c_{Na} = 0.8501$) with a thickness of 0.7 mm, at temperatures of 120, 135, 150, 170 and 190 ± 1 °C. Figure 1 gives two examples. The data at 80 and 100 °C were taken from Huijben *et al.*[1] We have chosen such a concentration that the dependence on W of $S_{CC}(0)$ is at maximum. So, we are looking for the maximum of the weighting factor in front of W in Eqs. (10) and (11). This optimalization results in $c_{Na} = 0.82$, nearly the same composition where $S(0)$ is at maximum (see Huijben *et al.*[2]).

Figure 2 shows the $S(0)$ values as a function of temperature. Note the usual decrease of $S(0)$ with increasing temperature. We can now calculate $S_{CC}(0)$ as a function of temperature using Eq. (12). For calculating the dilatation factor, the density measurements of Huijben *et al.*[10] were used. For the χ_T term a linear interpolation between the $S(0)$ values of the pure metals

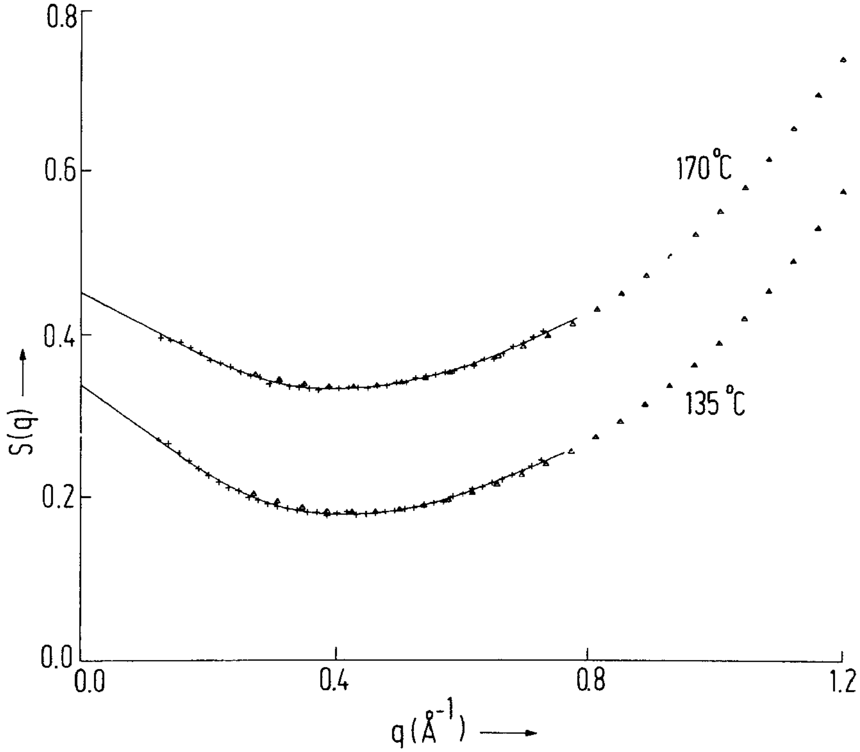

FIGURE 1 Small-angle part of the experimental x-ray structure factor $S(q)$ of the liquid alloy $Na_{0.85}Cs_{0.15}$. Temperatures are indicated in the figure. The zero of the ordinate of the upper curve is shifted upwards by +0.15: triangles, interpolations of larger-angle measurements; crosses, small-angle measurements; full curve, the best fit to the small-angle results. For $q < 0.12$ Å^{-1}, the measured structure factors have been obtained by extrapolation.

($S(0) = \rho_0 kT\chi_T$) has been substituted. This procedure is justified in the paper of Huijben *et al.*[1]

With the use of Eqs. (10) and (11) we can now calculate w and W. The results for W are displayed in Figure 3. All the numerical results involved are collected in Table I. We observe that $S_{CC}(0)$ decreases from 0.65 at 80 °C to 0.35 at 190 °C, the latter value being approximately three times the ideal value of $S_{CC}(0)$ for this alloy. ($S^{id}_{CC}(0) = c(1 - c) = 0.13$). Furthermore, we see that with an increase in temperature from 80 to 190 °C, $S(0)$ and $S_{CC}(0)$ decrease by about 45 %, W decreases only by 15 %, while w increases by 11 %.

The error in $S(0)$ is determined mainly by the extrapolation to $\mathbf{q} = 0$, and is estimated to be ± 10 % (Huijben *et al.*[1], Tamaki *et al.*[18]). It leads to an error of ±4 % in W, but because this is a systematic error, it would give rise to a still smaller one in $\partial W/\partial T$. The straight line in Figure 3 has been calculated by

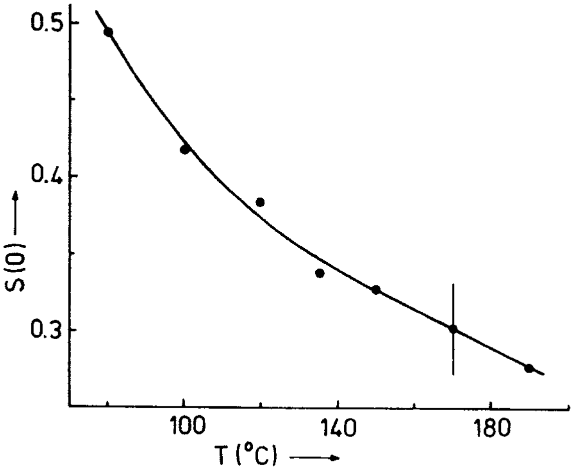

FIGURE 2 The experimental x-ray values of $S(0)$ for liquid $Na_{0.85}Cs_{0.15}$ as a function of the temperature T. The circles show our experimental results. Within the experimental error all the values coincide with the drawn curve.

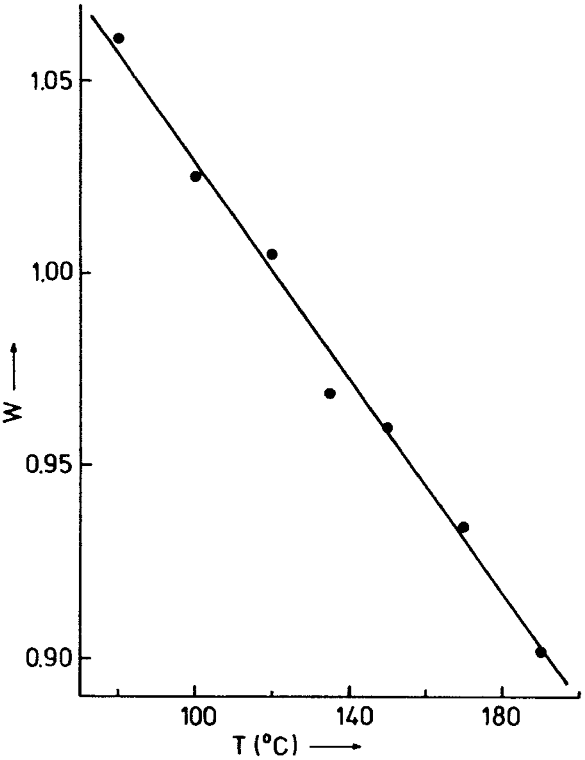

FIGURE 3 The interchange energy parameter W for liquid $Na_{0.85}Cs_{0.15}$ as a function of the temperature T. The circles show our experimental results, the straight line is the least squares fit to the points, given by $W(T) = 1.170 - 0.001408\ T$.

TABLE I

Values of $S(0)$, $S_{CC}(0)$, W and w for $Na_{0.85}Cs_{0.15}$ as a function of the temperature T. The values indicated by an asterisk are from Huijben *et al.*[1, 2]

T(°C)	$S(0)$	$S_{CC}(0)$	W	w(meV)
80	0.494*	0.654	1.061	32.29
100	0.417*	0.549	1.025	32.96
120	0.384	0.503	1.005	34.05
135	0.338	0.440	0.969	34.08
150	0.328	0.425	0.960	35.01
170	0.303	0.391	0.934	35.67
190	0.277	0.354	0.902	36.00

least squares fitting, which resulted in $W(T) = 1.170 - 0.001408t$ and $w(T) = 29.57 + 0.03501t$ (meV), with the temperature t in degrees Celsius.

To compare with the data of the enthalpy of mixing (Yokokawa and Kleppa[13]) we need the value of the interchange energy parameter at 111 °C. With $W' = (w - T\partial w/\partial T)/kT$ we find $W'(111) = 0.61 \pm 0.02$, to compare with $W' = W = 1.04$ in the case of a temperature independent w (Huijben *et al.*[1]). Using Eq. (8), the measurements of the enthalpy of mixing can be best described with $W' = 0.77 \pm 0.06$ for all concentrations. We see that a certain "overshoot" has occurred by introducing $\partial W/\partial T$ into the calculation: whereas first the x-ray results gave a higher value of W' than the calorimetric results, now the opposite is observed, although the discrepancy has decreased.

For the analysis of the EMF data on Na-Cs (Ichikawa *et al.*[14]) we make use of the formula $\varepsilon = -(RT \ln a_1)/F$, with ε the measured EMF, F the Faraday constant and a_1 the chemical activity of component 1. The activity points are fitted to the Flory model and we get W as a function of temperature. This method results at 110 °C in $W = 1.13$, $\partial W/\partial T = -0.00253\ \mathrm{K}^{-1}$ and $W' = 0.97$. Again we obtain a better agreement with the calorimetric result ($W' = 0.77$) by introducing a temperature dependence of W, although the improvement is far too small to compensate for the whole discrepancy.

Ichikawa *et al.*[14] calculated from their EMF experiments the enthalpy of mixing. For $c_{Na} < 0.5$ their results do agree quite well with the calorimetric results of Yokokawa and Kleppa.[13] For $c_{Na} > 0.5$, their values of $\Delta_m H$ are progressively lower than those of Yokokawa and Kleppa and at $c_{Na} = 0.85$, their value of $\Delta_m H = 465\ J/\mathrm{mol}$ implies $W' = 0.51$. These discrepancies can possibly be attributed to the inaccuracy introduced by determining $\partial\varepsilon/\partial T$; ε varies slowly in the sodium-rich region as a function of temperature and is rather small.

It is of interest to mention that the temperature dependence of $W(T)$ for Na-Cs obtained here is quite similar to that of two other alkali alloys, namely Na-K and Li-Na given by Bhatia *et al.*[6] and Ratti and Bhatia,[7] respectively, in their discussions on phase diagrams. Bhatia *et al.*[6] assumed, in a limited range of temperatures, a linear dependence of W on T and determined the coefficients from the free energy and enthalpy of mixing data at 300 K[19] using the regular solution model. Thus writing $W = W_0(1 - bT)$, where W_0 and b are constants and T absolute temperature, they found $W_0 = 1.9$ and $b = 0.00146\ \mathrm{K}^{-1}$. (More recent data at 384 K[20] gives $W_0 = 1.86$ and $b = 0.00127\ \mathrm{K}^{-1}$). For the Li-Na system, Ratti and Bhatia[7] found that the phase separation curve calculated using the Flory model was in much better agreement with experiment if the interchange energy was taken to be temperature dependent such that $W_0 \simeq 6.0$ and $b = 0.00135\ \mathrm{K}^{-1}$; the temperature range here is 400–600 K. For Na-Cs, $W(T)$ deduced above from the x-ray data means $W_0 = 1.55$ and $b = 0.00091\ \mathrm{K}^{-1}$.

Finally, we can conclude that introducing a temperature dependence of the interchange energy into the Flory model, results in a better agreement between the different experimental data. There is not yet a full consistency but some progress has been made.

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