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Structural modelling of liquid $\text{Na}_x\text{Cs}_{1-x}$ alloys using the reverse Monte Carlo method

T Arai¹ and R L McGreevy

Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan
and
ISIS Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire
OX11 0QX, UK

E-mail: arai@nda.ac.jp

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Abstract

The structures of liquid $\text{Na}_x\text{Cs}_{1-x}$ alloys have been modelled using the reverse Monte Carlo method on the basis of x-ray and neutron diffraction data. The partial structure factors and partial radial distribution functions obtained were consistent with previous work. The average coordination numbers and coordination number distributions for the four distinct kinds of atom pairs have been calculated over a wide range of composition. Cs forms complex clusters near 85 at.% Na, near to the maximum of the density fluctuation in these alloys.

1. Introduction

The composition dependence of the structural and physical properties of liquid alkali-metal alloys is an outstanding theoretical problem, although the properties of the elemental liquid metals are easily treated by pseudopotential theory [1]. Many investigations of liquid Na–Cs alloys have been performed since 1970. Some of the physical properties of these alloys have anomalous behaviour, especially their dependence on composition. The details have been summarized by Gartrell-Mills *et al* [2].

An early point of interest was the behaviour of the electrical resistivity [3–5]. Later, investigations of the structures and thermodynamic properties were reported. Huijben *et al* carried out neutron and x-ray diffraction measurements over a wide concentration range [5]. The behaviour of the concentration–concentration partial structure factor $A_{CC}(Q \rightarrow 0)$ is anomalous in that it peaks on the Na rich side, near to the composition $\text{Na}_{0.85}\text{Cs}_{0.15}$, which

¹ Author to whom any correspondence should be addressed. Present address: Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan.

Table 1. Experimental parameters used in the RMC modelling and first-neighbour coordination distances d_{ij} .

Na (at.%)	Temperature (°C)	ρ (\AA^{-3})	d_{NaNa} (\AA)	d_{NaCs} (\AA)	d_{CsCs} (\AA)
30	42	0.01076	5.9	6.3	7.2
50	50	0.0131	5.6	6.1	6.9
60	60	0.0145	5.5	6.2	6.8
75	75	0.0172	5.3	6.0	6.7
85	80	0.0195	5.4	5.9	6.4
90	100	0.0209	5.2	5.7	6.7
95	100	0.0224	5.2	5.6	6.6

it has been suggested might be due to the existence of the compounds Na_2Cs or Na_3Cs . Alternatively it may indicate a large concentration fluctuation near this composition and imply that the system has a tendency to phase separation in the liquid state.

It is known that there is no thermodynamic or other evidence of actual phase separation in the liquid state of these alloys [2, 3, 6]. However, it has been suggested that there is a strong tendency to phase separation on the Na rich side. Bowles *et al* have explained the global features of $A_{CC}(Q \rightarrow 0)$ using the Bhatia–Young model [7]. However, since the coexistence of separated liquid phases has not been observed, we will use the term ‘complex formation’ instead of ‘tendency to phase separation’.

The reverse Monte Carlo (RMC) method has been described in detail elsewhere (e.g. [8, 9]). It offers the possibility of modelling the structure of this two-component system on the basis of the combination of x-ray and neutron diffraction data. The aim of our study is to reveal the local structure near the large density fluctuation, that is the complex formation in liquid $\text{Na}_x\text{Cs}_{1-x}$ alloys near the solidus line, on the basis of the measured structure factors. In this work we use the total structure factors which have been measured by Huijben *et al*, by both means of x-ray and neutron diffraction, covering the whole composition range [4, 5]. Calculating properties from the three-dimensional atomic configurations obtained, we show some structural properties related to the local structure in order to obtain insight into the complex formation that occurs near the larger density fluctuation.

2. RMC modelling

We have used structure factor data for 30, 50, 60, 75, 85, 90 and 95 at.% Na, at 373 K for both x-ray and neutron diffraction. Relevant parameters used in the modelling are given in table 1. Modelling was started at the composition $\text{Na}_{0.3}\text{Cs}_{0.7}$. To make the initial configuration for this model, we used a model for pure liquid Cs near the melting point obtained from a molecular dynamics (MD) simulation using an empirical potential [10]. The model consisted of 4096 atoms in a cubic box with periodic boundary conditions. We randomly selected an appropriate number of atoms in the Cs model and replaced them by Na, then changed the density to the correct experimental value (as given in table 1). We constrained the partial radial distribution functions as follows: $g_{\text{NaNa}}(r) = 0$ for $r < 3.0 \text{ \AA}$, $g_{\text{NaCs}}(r) = 0$ for $r < 3.3 \text{ \AA}$ and $g_{\text{CsCs}}(r) = 0$ for $r < 3.6 \text{ \AA}$. These values are consistent with MD results [5]. After several million atomic moves, the final configuration for the $\text{Na}_{0.3}\text{Cs}_{0.7}$ model was used as the initial configuration for the $\text{Na}_{0.5}\text{Cs}_{0.5}$ model, with suitable random substitution of Na for Cs. In the same way we iteratively created the initial and final configurations for all compositions.

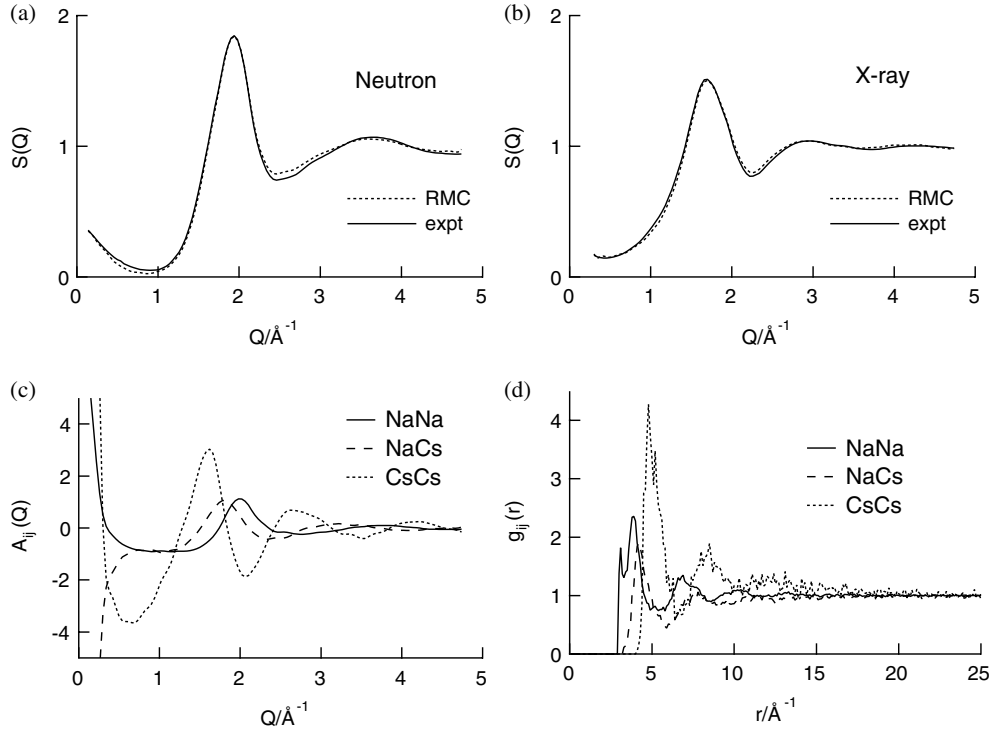


Figure 1. Results for liquid $\text{Na}_{0.85}\text{Cs}_{0.15}$. Experimental total structure factors, $S(Q)$, (solid curves) and RMC model fits (broken curves) for (a) neutron diffraction and (b) x-ray diffraction. (c) The corresponding partial structure factors, $A_{ij}(Q)$, and (d) partial radial distribution functions, $g_{ij}(r)$.

3. Results and analysis

Typical results of fits to two experimental structure factors are shown in figure 1. The partial structure factors combine to agree well with the total structure factors of both neutron and x-ray data. However, RMC modelling produces a rather sharp peak on the low r side of the first peak in $g_{\text{NaNa}}(r)$. This is probably due to small systematic errors in the experimental data; e.g. the x-ray data appear to have a very slight downwards slope. However, we judge that this does not significantly influence the main results discussed.

From the partial structure factors $A_{\text{NaNa}}(Q)$, $A_{\text{NaCs}}(Q)$ and $A_{\text{CsCs}}(Q)$ obtained from the RMC models we have calculated the Bhatia–Thornton number (N) and concentration (C) partial structure factors:

$$A_{NN}(Q) = c_1^2 A_{11}(Q) + c_2^2 A_{22}(Q) + 2c_1 c_2 A_{12}(Q)$$

$$A_{CC}(Q) = c_1 c_2 [1 + c_1 c_2 \{A_{11}(Q) + A_{22}(Q) - 2A_{12}(Q)\}]$$

where $A_{ij}(Q)$ are the Faber–Ziman partial structure factors and c_i is the concentration of species i . $A_{CC}(Q)$ and $A_{NN}(Q)$ for all alloy concentrations are shown in figure 2. It appears that $A_{CC}(Q \rightarrow 0)$ has a maximum near to the composition $\text{Na}_{0.85}\text{Cs}_{0.15}$. This is consistent with previous work [5].

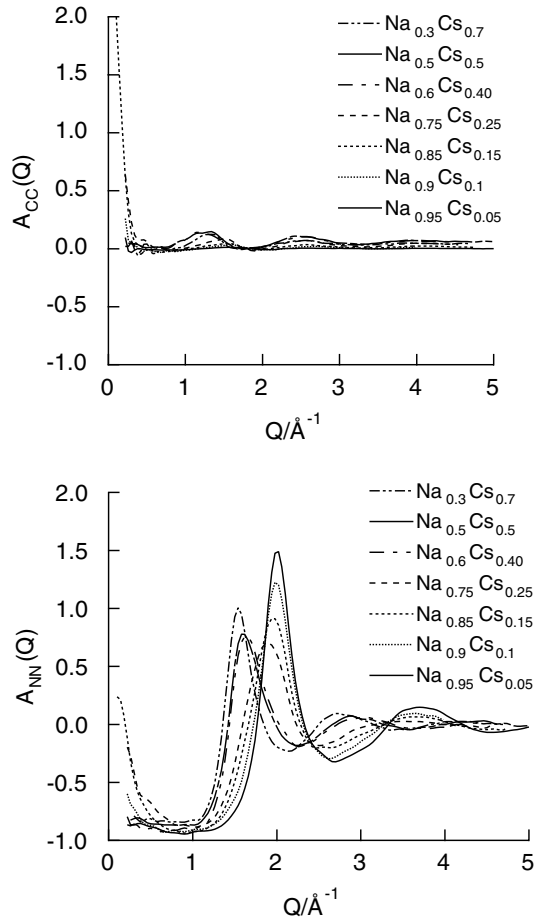


Figure 2. Bhatia–Thornton partial structure factors $A_{CC}(Q)$ and $A_{NN}(Q)$ for 30, 50, 60, 75, 85, 90 and 95 at.% Na.

It is not so easy to understand the real atomic structure from one-dimensional functions. We have determined the average coordination number \tilde{n}_{ij} and coordination number distribution $D(n_{ij})$ as a function of coordination number n_{ij} for each species from the three-dimensional configurations (n_{ij} being the number of j atoms coordinated with a central i atom). We have defined maximum first-nearest neighbour distances d_{ij} for Na–Na, Cs–Cs and Na–Cs from the position of the first minimum after the first peak of $g_{ij}(r)$. These values are listed in table 1.

First, we show \tilde{n}_{ij} as a function of Na concentration in figure 3. Average coordination numbers for liquid pure Na and Cs near their melting points are also plotted, taken from the results of previous works [10, 11]. \tilde{n}_{ij} for all ij pairs changes almost linearly with Na concentration, although there is a small kink near $x = 0.85$. \tilde{n}_{CsNa} is only slightly smaller than \tilde{n}_{NaNa} for almost all compositions, but \tilde{n}_{CsCs} is always larger than \tilde{n}_{NaCs} . This means that these alloys are not homogeneous on the atomic scale. It can also be noted that in the limit of low Cs concentration, i.e. $x \rightarrow 1$, $\tilde{n}_{CsCs} \rightarrow 2$.

From these results we can say that the increase in $S(Q \rightarrow 0)$ for low Cs concentrations (i.e. low Cs densities) is caused by density fluctuations of the Cs atoms. This behaviour is

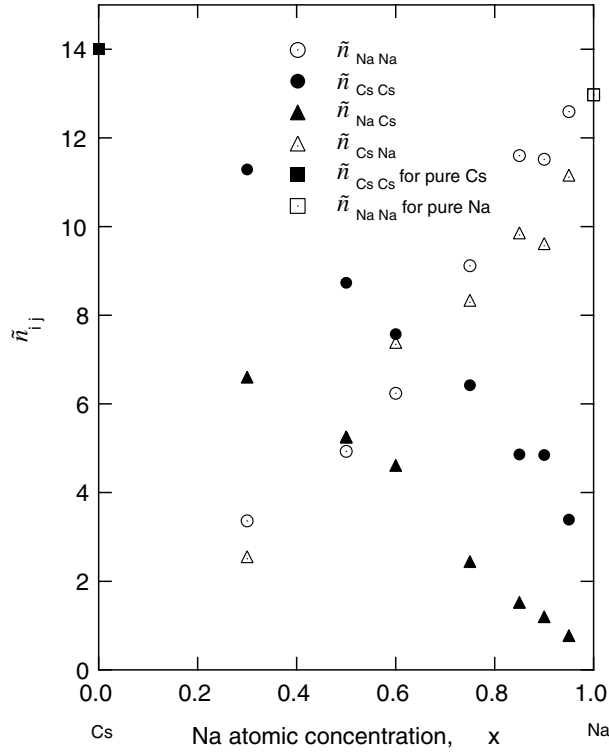


Figure 3. Changes in average coordination number as a function of Na concentration. The nearest neighbour distances d_{ij} are taken from the first minimum in the respective $g_{ij}(r)$ and are given in table 1. The coordination numbers for pure Cs and Na are calculated from MD results obtained using empirical potentials [11, 13].

similar to that of expanded Cs near the critical point [12]. However, Cs atoms in NaCs alloys seem to be relatively compressed due to the existence of the surrounding Na atoms.

Figure 4 shows the normalized distributions of coordination numbers, $D(n_{ij})/\tilde{n}_{ij}$. Note that at the lowest Cs concentration $D(n_{\text{NaCs}})$ is non-zero up to $n_{\text{NaCs}} = 7$, i.e. some Na have a surprisingly large number of Cs neighbours, and correspondingly $D(n_{\text{CsCs}})$ peaks at $n_{\text{CsCs}} = 3$. Both of these indicate an apparent tendency for Cs to cluster. This is clearly seen in the picture of a $\text{Na}_{0.85}\text{Cs}_{0.15}$ configuration shown in figure 5. Molecular dynamics simulation [5] shows a similar tendency for Cs to cluster, though to a much lesser extent.

We have tested the ‘reachability’ of Cs clusters, which means whether the clusters connect from one side of the cubic box to the opposite side along any of the three axes. This is a kind of percolation function which is calculated in the same way as in previous work [12]. We find that the Cs clusters percolate across the configuration up to $x = 0.85$, which is significantly higher than would be expected for a random distribution, but not for $x > 0.85$. This may be the explanation of the maximum value of $S(Q \rightarrow 0)$ at this composition. However, it is clear that this is not really a tendency to phase separation, in that the tendency is rather for Cs to maintain a connected network. The reason for this is not obvious. It might be considered that there should be some noticeable effect on the electrical resistivity. While ρ shows no particular effects, and $d\rho/dT$ peaks anomalously but at $x \sim 0.74$ [13], the normalized temperature derivative of the resistivity $(1/\rho)(d\rho/dT)$ clearly deviates from the expected behaviour around $x = 0.85$, as

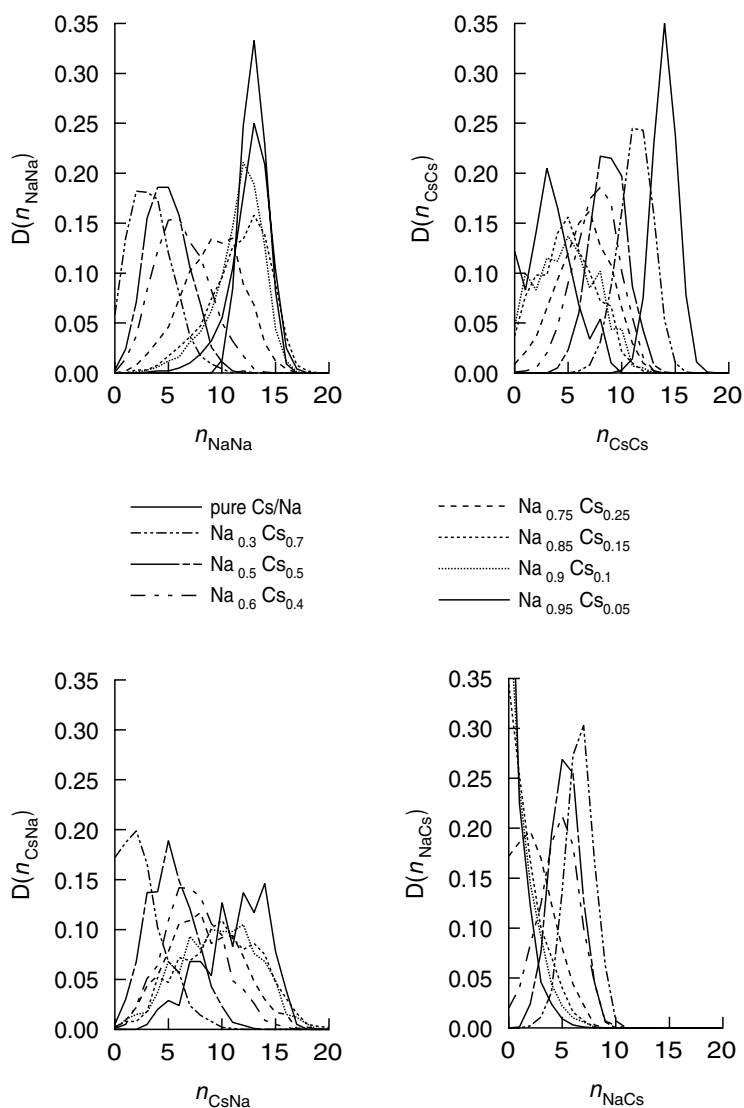


Figure 4. Normalized coordination number distributions $D(n_{ij})/\bar{n}_{ij}$, for Na–Na, Cs–Cs, Cs–Na and Na–Cs. The distributions for pure Cs and Na are calculated from MD results obtained using empirical potentials [11, 13].

shown in figure 6. The origin of this behaviour in terms of the relevant electronic states could be tested by *ab initio* simulation.

4. Conclusions

Reverse Monte Carlo modelling has been used to study the structure of liquid NaCs alloys on the basis of the combination of x-ray and neutron diffraction data. These alloys are not microscopically homogeneous. The density fluctuation is largest near the composition $\text{Na}_{0.85}\text{Cs}_{0.15}$. At this composition the average coordination numbers and coordination number

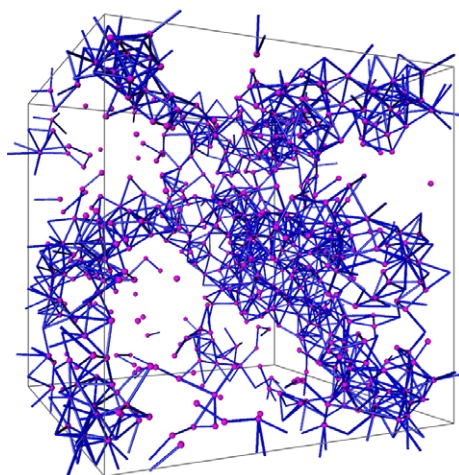


Figure 5. Bonds between Cs atom pairs within $d_{\text{CsCs}} = 6.6 \text{ \AA}$ for liquid $\text{Na}_{0.85}\text{Cs}_{0.15}$.

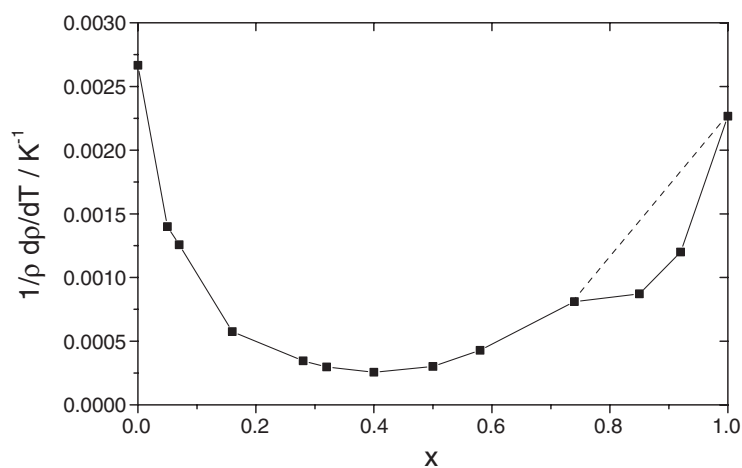


Figure 6. Experimental values of $(1/\rho)(\text{d}\rho/\text{d}T)$ for liquid $\text{Na}_x\text{Cs}_{1-x}$ alloys at $T = 373 \text{ K}$ [13]. The dashed curve indicates the type of behaviour that might be expected purely from atomic size effects.

distribution have an anomalous behaviour due to complex formation. This composition appears to be close to a percolation transition for Cs clusters.

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