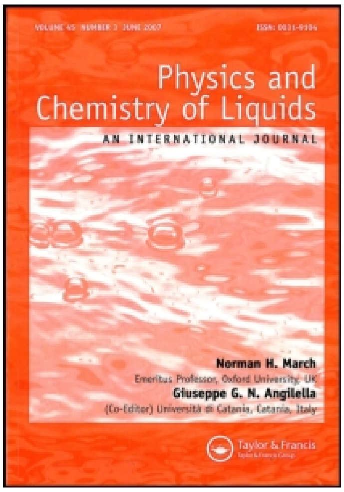

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Short-range Ionic Correlations in Gold-Cesium Melts

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1 INTRODUCTION

The molten gold-cesium system has received considerable attention as an example[1–3] of a liquid alloy which, though formed from metallic elements, exhibits non-metallic behaviour near stoichiometry. A stoichiometric solid compound CsAu, which has semiconducting properties and some degree of ionic binding, with gold playing the role of the negative constituent, has been known for a long time.[4] The liquid structure of the system has been extensively studied by neutron diffraction by Martin *et al.*[5–7] over a range of composition going from stoichiometry to pure cesium metal. Since the neutron scattering amplitudes of the two components are not very different, the observed diffraction pattern is mainly determined by the overall liquid

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structure and cannot display very strikingly the relative ordering of the constituents. Nevertheless, a broad hump is present near stoichiometry on the low-k side of the main peak in the diffraction pattern, which indicates[6,8] a marked preference for unlike nearest neighbours as in a molten ionic material.[9] At cesium concentrations between 60 and 80 at %, on the other hand, a strong enhancement of the small-angle scattering intensity is observed, which reflects[7] a tendency to segregation over a length scale of several Angstroms.

It is clear from the available evidence[3] that, even at stoichiometry, this liquid system cannot be described in quantitative detail by a simple ionic model such as is applicable[10] to molten alkali halides. As one moves towards the cesium-rich side of the phase diagram, furthermore, the role of the outer electrons should become increasingly important in determining the behaviour of ionic correlations in the small-angle scattering region, as is the case[11] for the liquid alkali metals. On the other hand, the main-peak region of the diffraction pattern should carry information on the interactions which determine the short-range ionic correlations in the liquid. With this limited scope the present work thus examines the available structural evidence. The gross questions that we ask are (a) what values of ionic valences and ionic radii are consistent with this evidence at stoichiometry and (b) how far do such values apply as one moves away from stoichiometry.

2 IONIC RADII

It is useful before examining the structural data to obtain some independent orientation on the likely values for the ionic diameters that are appropriate to various states of the cesium and gold ions. In the range of composition of present interest these are first of all the diameters of the Cs^+ ion in an ionic liquid and in a metallic liquid. The corresponding values can be estimated from previous work on the structure of molten cesium halides[10] and of liquid alkali metals[11,12] to be $\sigma_{Cs^+}^{ion} \simeq 3.2$ Å and $\sigma_{Cs^+}^{met} \simeq 4.3$ Å, respectively, at the temperature $T \simeq 600°C$ of present interest. Of course, $\sigma_{Cs^+}^{ion}$ measures the size of the ionic core of the cesium ion, while $\sigma_{Cs^+}^{met}$ is essentially determined by the ion-ion Coulomb repulsion in the sea of conduction electrons.

The value of $\sigma_{Cs^+}^{ion}$ that we have estimated above happens to be quite close to the Pauling[13] ionic diameter, $\sigma_{Cs^+}^{P} = 3.38$ Å. It thus seems reasonable to use the Pauling ionic diameter of gold, $\sigma_{Au^+}^{P} = 2.74$ Å, to get an estimate $\sigma_{Au^+} \simeq 2.7$ Å for the size of the inner ionic core of the gold ion for our present purposes.

The size of the Au^- ion, on the other hand, may be expected to be measured by a rough value $\sigma_{Au^-} \approx 4$ Å for the diameter. This follows from the Cs–Au distance in the stoichiometric CsAu compound,[4] $d_{Cs-Au} = 3.69$ Å, after subtraction of an ionic radius for Cs^+ of 1.6 ÷ 1.7 Å. Recent calculations[14] of the density distribution for the outer $(6s)^2$ electrons on the Au^- ion in the same compound are consistent with this estimate. Finally, the Pauling diameter for the I^- ion in an ionic compound, $\sigma^P_{I^-} = 4.32$ Å, again suggests the same rough value for σ_{Au^-}.

With this preliminary and admittedly rough orientation on the values of these parameters, which are collected for convenience in Table I, we now turn to the liquid structure data.

TABLE I

Ionic diameters for the Au–Cs liquid system (Å)

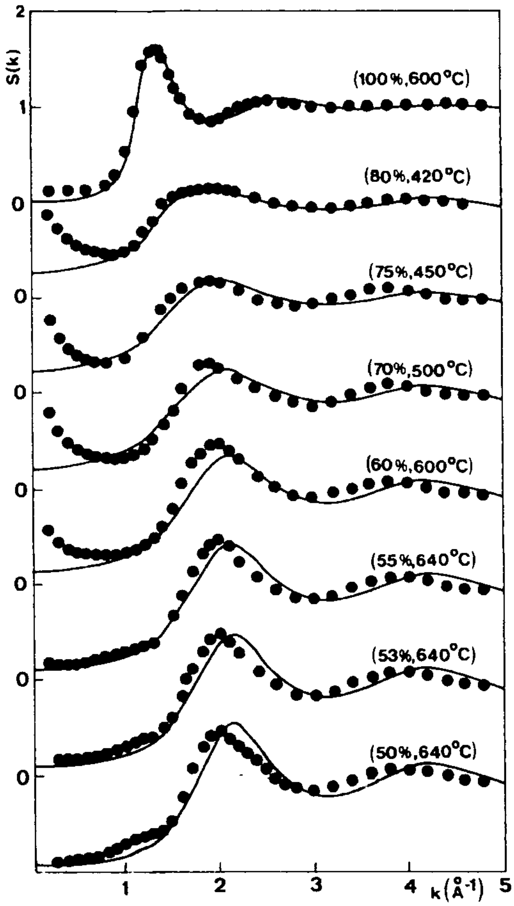
	ionic core	metallic
Cs	3.2	4.3
	inner ionic core	outer $(6s)^2$ configuration
Au	2.7	4.

3 DIFFRACTION PATTERN

The calculations of the diffraction pattern of the liquid alloy at various concentrations that are reported below have been based on the mean spherical approximation for a mixture of charged hard spheres on an inert neutralizing background.[15] The density of the liquid at various temperatures and compositions has been taken from the data of Martin *et al.*[16]

We consider first the case of stoichiometric composition, where a simple ionic model would require according to our previous discussion $\sigma_{Cs} \simeq 3.2$ Å and $\sigma_{Au} \simeq 4$ Å, with valences $Z_{Cs} = +1$ and $Z_{Au} = -1$, respectively. This model leads to violent disagreement with experiment. For instance the height of the main peak in the diffraction pattern $S(k)$ (defined as in the original experimental work[6]) turns out to be about 4, against an observed value of somewhat less than 1.5. The disagreement is not unexpected, as we remarked in the introduction, since one is dealing with a semiconductor rather than with an ideal ionic material.

As is shown in the bottom drawing in Figure 1, however, one can obtain reasonable agreement with the observed diffraction pattern in the region of the main peak by simply allowing for a much smaller value of the ionic diameter of gold—indeed by taking a value 2.7 Å for this diameter, as we estimated above for the size of the inner core. This suggests that, while the long range interactions conform to an ionic model as indicated by the values $Z_{Cs} = +1$ and $Z_{Au} = -1$, the outer $(6s)^2$ configuration of the gold ion is



Diffraction pattern of gold-cesium liquid alloy at various compositions and temperatures. Full curves: theoretical results; dots: experimental data from Martin *et al.*, Refs. 5 and 6. The parameters in the calculations at finite gold concentration are $Z_{Cs} = +1$, $Z_{Au} = -1$, $\sigma_{Au} = 2.7$ Å and $\sigma_{Cs} = 3.20$ Å at 600°C (with a weak temperature dependence estimated from Ref. 10). The upper curve refers to pure cesium metal and uses $\sigma_{Cs} = 4.30$ Å.

very soft and steep repulsive interactions arise only when the inner cores come into play. This model is also in qualitative agreement with experiment in presenting a broad hump in the diffraction pattern around $k \sim 1.1$ Å^{-1}.

The other drawings in the figure show that the same crude model, with the same values for the ionic diameters and valences, yields reasonable agreement with experiment up to a cesium concentration of 80 at %, except in the small-angle scattering region. Only in the uppermost drawing, which refers to pure cesium metal, has the diameter of cesium been taken to have its metallic-state value of 4.3 Å. It thus appears that the liquid alloy, over the whole range of (finite) gold concentration explored by the experiments, has short-range order appropriate to an ionic liquid as far as the available concentration of gold will allow.

It is also interesting to notice that the small-angle scattering, which in our qualitative interpretation reflects the screening properties of the excess conduction electrons away from stoichiometry, begins to build up in the experiments only above a threshold of 55 ÷ 60 at % cesium. This seems consistent with the observation[2] of a localized-electron behaviour over a finite range of composition around stoichiometry.

4 SUMMARY

Neutron diffraction data on gold-cesium liquid alloys can be qualitatively interpreted by an ionic model for short-range correlations, the gold constituent being in a negative-ion state with a very soft outer-electron configuration. The small-angle scattering region reflects on the other hand, the detailed screening effects of the excess outer electrons in the non-stoichiometric systems.

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