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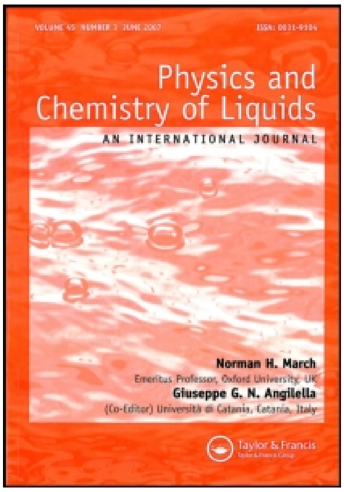

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# Structure and Density of Gold-Cesium-Melts

## III. Neutron Diffraction with Au-Cs-Melts in the small *q* Region

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## INTRODUCTION

During the performance of neutron diffraction experiments with Au-Cs-melts as described in Ref. 1 a scattering effect was observed in the small *q* region, which now shall be treated in detail.

## THEORETICAL BACKGROUND

According to Bhatia and Thornton, Ref. 2, the following relationship exists between the differential coherent scattering cross section per atom $(1/N)\mathrm{d}\sigma/\mathrm{d}\Omega|_{\mathrm{coh}}\,(q)$ and the partial structure factors $S_{\mathrm{NN}}$, $S_{\mathrm{CC}}$, and $S_{\mathrm{NC}}$:

$$\frac{1}{N}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\bigg|_{\mathrm{coh}}(q) = \langle b\rangle^2 S_{\mathrm{NN}}(q) + (\Delta b)^2 S_{\mathrm{CC}}(q) + 2\langle b\rangle(\Delta b) S_{\mathrm{NC}}(q) \qquad (1)$$

The symbols have the same meaning as described in Ref. 1. For the long wavelength limit ($q = 0$) the three partials can be described by thermodynamical data[2] and we obtain from Eq. (1):

$$\frac{1}{N}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\bigg|_{\mathrm{coh}}(0) = \rho_0 k_B T K_T \langle b\rangle^2 + S_{\mathrm{CC}}(0)[\theta\langle b\rangle - \Delta b]^2 \qquad (2)$$

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with

$$\begin{aligned}\rho_0 &= \text{mean atomic number density}\\ k_B &= \text{Boltzmann's constant}\\ T &= \text{absolute temperature}\\ K_T &= \text{isothermal compressibility}\\ S_{CC}(0) &= Nk_B T/(\partial^2 G/\partial c^2)_{p,T,N} \qquad (3)\\ \theta &= 1/V_M(\partial V_M/\partial c_1) = \text{dilatation factor}\\ V_M &= \text{molar volume}\\ G &= \text{free enthalpy}\end{aligned}$$

We obtain $S_{CC}(0)$ either by Eq. (3) from thermodynamical data or by Eq. (2) from the intensity of scattered neutrons extrapolated to $q = 0$ if the dilatation factor $\theta$ and the isothermal compressibility $K_T$ are known.

For the statistical distribution of the atoms of both kinds stands $S_{CC}(0) = c_1c_2$, for tendency to compound formation $S_{CC}(0)$ lies between $c_1c_2$ and zero, for tendency to segregation $S_{CC}(0)$ becomes larger than $c_1c_2$. For a miscibility gap in a binary phase diagram $S_{CC}(0)$ diverges going from the single phase to the two phase region at a certain temperature $T_c$ and a certain concentration $c_c$. Near this critical point the temperature dependency of $S_{CC}(0)$ is described as follows:

$$S_{CC}(0) = k_B T \varepsilon^{-\gamma} \qquad (4)$$

with

$$\begin{aligned}\varepsilon &= (T - T_c)/T_c\\ \gamma &= \text{critical exponent}\end{aligned}$$

Critical scattering first was described by Ornstein and Zernike[3] for one component liquids and this method was transferred by Stanley[4] to the submicroscopical concentration fluctuations in binary melts. According to this method $S_{CC}(q)$ in the region of small $q$'s behaves like a Lorentz curve:

$$S_{CC}(q) = \frac{S_{CC}(0)}{1 + \xi^2 q^2} \qquad (5)$$

$\xi$ is the correlation length, i.e. a measure for the extension of concentration fluctuations. The Ornstein–Zernike plot ($S_{CC}^{-1}(q)$ vs. $q^2$) normally yields a straight line whose gradient $a$ and axis intercept $b$ are necessary to calculate the correlation length $\xi$:

$$\xi = \sqrt{\frac{a}{b}} \qquad (6)$$

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According to Ref. 4 the temperature dependency of $\xi$ is described by an expression similar to Eq. (4):

$$\xi = \xi_0 \left( \frac{T - T_c}{T_c} \right)^{-\nu} \tag{7}$$

$\nu$ is also a critical exponent.

Analogous to Eq. (2) the $q$-dependence of the scattered intensity for small $q$'s follows Eq. (8).

$$\frac{1}{N} \frac{d\sigma}{d\Omega}\bigg|_{\mathrm{coh}} (q) = A(q) \rho_0 k_B T K_T \langle b \rangle^2 + S_{CC}(q) [\theta \langle b \rangle - \Delta b]^2 \tag{8}$$

with

$$A(q = 0) = 1$$

We know from the experiments with pure elements for which $S_{CC}(0) = 0$, $A(q)$ for $q < 0.5$ Å$^{-1}$ to be nearly independent of scattering angle and thus being equal to $A(0)$.

Using the abbreviation

$$I(q) = S_{CC}(q) [\theta \langle b \rangle - \Delta b]^2 \tag{9}$$

from Eqs. (4) and (5) we obtain

$$I(q) = \frac{I(0)}{1 + \xi^2 q^2} \tag{10}$$

and

$$I(0) = \text{const.}\ T \left( \frac{T - T_c}{T_c} \right)^{-\gamma} \tag{11}$$

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## EXPERIMENTS, RESULTS, AND DISCUSSION

In Ref. 1 we have described scattering experiments with Au-Cs-melts at 600°C using neutrons with wavelength 0.692 Å. For the concentrations 60, 70, and 75 at % Cs an increase of scattered intensity was observed for small $q$'s. The term $\rho_0 k_B T K_T \langle b \rangle^2$ within Eq. (8) had to be estimated as follows, since no experimental compressibilities were available: the $(1/N) d\sigma/d\Omega|_{\mathrm{coh}}(q)$-curves calculated for the so called segregation model in Ref. 1 were in good accordance with the experimental run for $q \geq 1$ Å$^{-1}$. Under the assumption that the compressibility term in the intermediate range between Cs and AuCs may be modelled by this segregation description, the term $\rho_0 k_B T K_T \langle b \rangle^2$ was

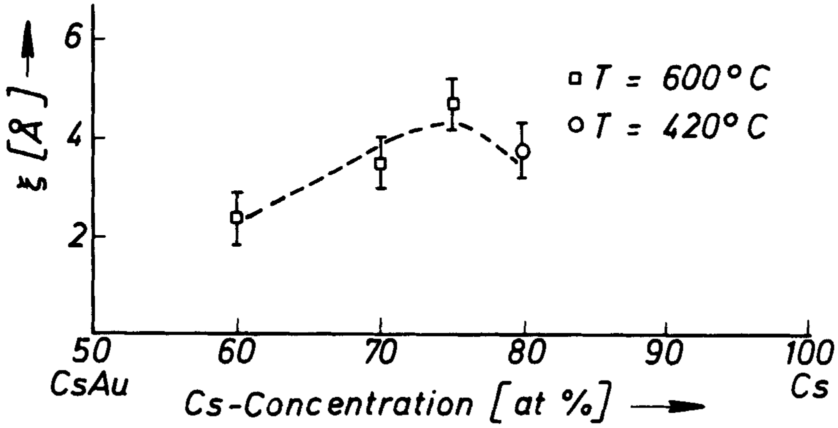

FIGURE 1 Au-Cs-melts: concentration dependency of the correlation length.

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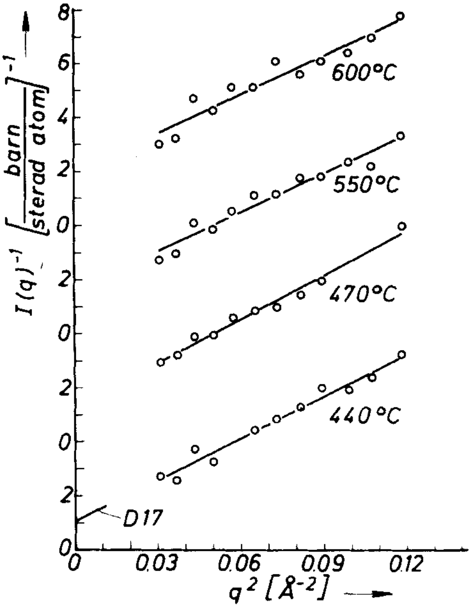

FIGURE 2 Au-Cs-melt containing 75 at % Cs: Ornstein-Zernike plots.

calculated from these model curves at small $q$'s. So $I(q)$ could be calculated from the measured coherent cross section using Eqs. (8) and (9). The Ornstein–Zernike plots obtained for $0.17\ \text{Å}^{-1} \leq q \leq 0.35\ \text{Å}^{-1}$ according to Eq. (10) yielded finally the correlation lengths plotted in Figure 1 vs. the concentration.

The value at 80 at% Cs was obtained at a temperature of 420°C. According to Eq. (7) it would be expected to be smaller for 600°C.

From Figure 1 we learn the correlation length to show a maximum for 75 at% Cs. Therefore the temperature dependence was studied using the corresponding melt between 440 and 600°C.

The Ornstein–Zernike method was applied to the normalized intensity. Thereby the term $\rho_0 k_B T K_T \langle b \rangle^2$ within Eq. (8) was slightly varied in such a way that the Ornstein–Zernike plots became straight lines for $0.03\ \text{Å}^{-2} \leq q^2 \leq 0.12\ \text{Å}^{-2}$.

In Figure 2 the measured points are presented together with straight lines fitted according to the least squares method.

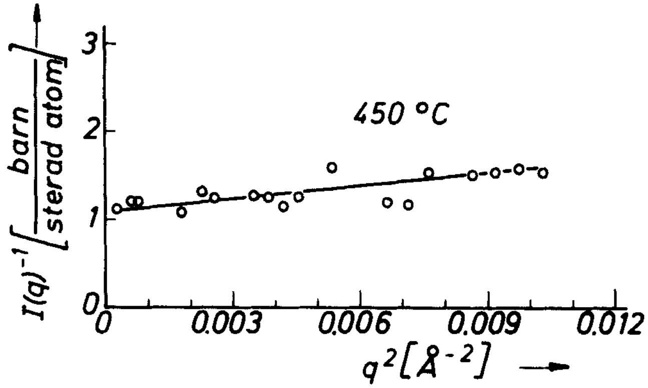

FIGURE 3 Au-Cs-melts containing 75 at% Cs: Ornstein–Zernike plot.

The line designed [ ] at the ordinate axis should be $[\ \ ]^{-1}$ in Figure 2 with "D17" is shown in Figure 3 using an enlarged scale. It was obtained from a melt containing 75 at % Cs at 450°C using long-wavelength (7.9 Å) neutrons at the special small angle scattering Instrument D17 of the ILL (Grenoble). The specimens were flat with a thickness of 2 mm and an irradiated area of $10 \times 2\ \text{mm}^2$. The container was made from a molybdenum foil 0.15 mm thick. The specimen-counter-distance amounted to 282 cm. The correlation length obtained was 7 Å which is in accordance with the value measured with the D4-instrument.

As was shown in Ref. 5, the Eqs. (7) and (11) are valid still far above the critical temperature. For $T \gg T_c$ the constants $\gamma$ and $\nu$ approach 1 and 0.5

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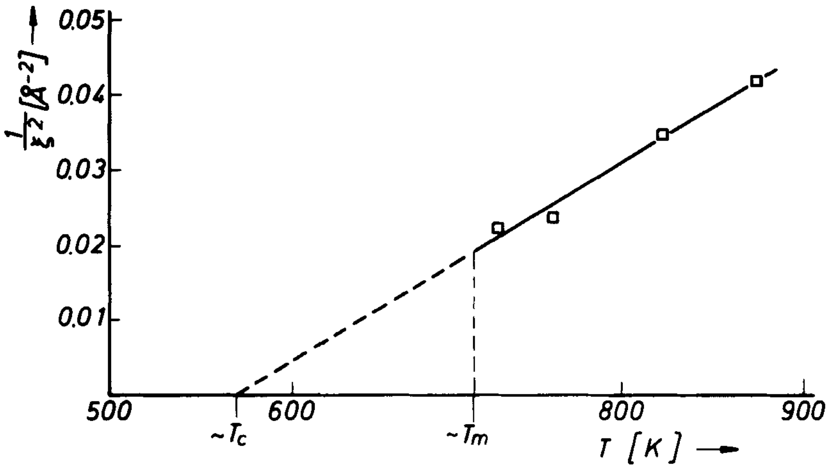

FIGURE 4 Au-Cs-melt containing 75 at % Cs: Temperature dependency of $\xi$.

as demanded by the mean field theory. Thus it is not surprising to obtain a linear behaviour by plotting $\xi^{-2}$ vs. $T$ as shown in Figure 4.

From the intersection of the extrapolated curve in Figure 4 with the abscissa we obtain using Eq. (7) with $\nu = 0.5$ the critical temperature $T_c = 570$ K, which lies below the liquidus line.

According to Eq. (11) we plotted log $TI(0)$ vs. log $(T - T_c)/T_c$, as shown in Figure 5 and obtain $\gamma = 1$ which is to be expected according to the classical theory.

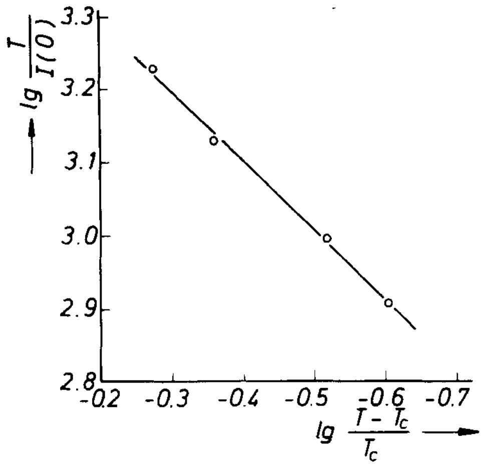

FIGURE 5 Au-Cs-melt containing 75 at % Cs: Determination of $\gamma$.

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Now we will compare the results of neutron small angle scattering obtained with the melts of the system AuCs-Cs with alkali metals solved in molten alkali halides. First of all it must be stated that the original phase diagram of the Au-Cs-system given in Ref. 6 proved to be wrong. Thus it was reinvestigated with the result[7] that the liquidus line shows a flatter run between 60 and 80 at% Cs. Thus the critical temperature evaluated during the present work lies indeed 140°C below the liquidus line in the region of the supercooled melt.

According to Ref. 8 the LiF-Li-system shows a distinct miscibility gap in the molten state. This gap becomes smaller going from NaF-Na to KF-K and finally to RbF-Rb. For the CsF-Cs-system, finally, it has vanished completely. Also with the other Cesiumhalide-Cesium-systems such as CsCl-Cs, CsBr-Cs, and CsJ-Cs no miscibility gap occurs. Since furthermore in these systems according to Ref. 8 the critical point lies below the corresponding liquidus line we state a close relationship between the AuCs-Cs-system and the mentioned Cesiumhalide-Cesium-systems.

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## SUMMARY

The Cs-rich Au-Cs-melts yield neutron small angle scattering for $q < 1$ Å$^{-1}$ which has its origin in a segregation tendency. This means the existence in the average of time of regions containing salt like $Au^-Cs^+$ and those containing metallic Cs.

This segregation effect can be described by concentration fluctuations with a certain correlation length. The concentration-dependent determination of the correlation length showed a maximum for the 75 at% Cs melt. Just this composition was investigated at different temperatures with the result that the critical temperature of the concentration fluctuations lies below the liquidus line in analogy to the Cesiumhalide-Cesium-systems.

## References (Part III)

1. W. Martin, W. Freyland, P. Lamparter, and S. Steeb, *J. Phys. Chem. Liq.*, **10**, 61 (III) (1979) (II).
2. A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).
3. L. S. Ornstein and F. Zernike, *Phys. Z.*, **19**, 134 (1918).
4. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford (1971).
5. H. Ruppersberg and W. Knoll, *Z. Naturforschung*, **32a**, 1374 (1977).
6. R. P. Elliot, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill Book Co., New York (1965).
7. D. Eschenweck, Dissertation, Universität Stuttgart (1979)
8. M. A. Bredig, *Molten Salt Chemistry*, Editor: M. Blander, Interscience, New York (1964).