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Structure and Density of Gold-Cesium-Melts

I. Neutron Diffraction with Gold- and with Cesium-Melts

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INTRODUCTION

In part I of the present publication we describe the scattering experiments performed using hot neutrons with Cs-melts and with Au-melts. Since Cs as well as Au show large neutron absorption cross sections and since furthermore the tabulated incoherent scattering cross section of Cesium proved to be wrong, it seemed necessary to decide by new scattering experiments between the discrepancies of former papers.

EXPERIMENTS

Neutron diffraction experiments were performed using the two axis diffractometer D4 at the high flux reactor of the Laue-Langevin-Institute, Grenoble.¹ This neutron source yields besides high flux also neutrons with rather high energy which emerge from a hot source ($T = 2000$ K). Thus the ratio of scattering cross section to absorption cross section ($\sigma_{\text{abs}} \sim \sqrt{1/E_{\text{Kin}}}$) is improved. The wavelength of the neutrons was $\lambda = 0.692$ Å. The $q = 4\pi \sin \theta/\lambda$ -region reached from 0.18 Å⁻¹ up to 10 Å⁻¹. The measurement for one specimen lasted at least 20 hours, thus the statistical error at large q -values was kept below ± 1 %. The furnace consisted of a vacuum vessel containing a vanadium tube which was heated by direct current.

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Since Cesium shows appreciable chemical aggressiveness, the preparation of specimens was very tedious since all the work had to be performed in ultrapure Argon or in vacuum. The specimen containers consisted of 0.1 mm Vanadium-foil, from which cylinders with outer diameter of 7 mm were made by electron beam welding. After filling in the corresponding specimen material, the cylinders were welded completely. The temperature measurement was done by a thermocouple fixed to the bottom of the container.

For the investigation of the Au-melt at 1100°C a container made from polycrystalline Al_2O_3 (wall thickness 0.55 mm, inner diameter 6.5 mm) was used.

The diffraction experiments were done in transmission.

CORRECTION FOR ABSORPTION AND FOR SCATTERING FROM FURNACE AND CONTAINER

To obtain the intensity diffracted by the specimen only, the total scattered intensity must be corrected for the absorption as well as for scattering by the furnace and by the container and for selfabsorption in the specimen. We used a formula proposed by Poncet,² who improved the formalism according to Paalman and Pings³ by taking care of the scattering and absorption of the heating tube. One of the important parameters thereby is the linear attenuation coefficient μ , which can be calculated as follows:

$$\mu = \rho_0 \sigma_t \quad (1)$$

with

$$\rho_0 = \frac{D \cdot N_A}{M} \quad (2)$$

$$\sigma_t = \sigma_{\text{coh}} + \sigma_{\text{inc}} + \sigma_{\text{abs}} \quad (3)$$

M = atomic weight

D = macroscopic density

N_A = Avogadro's number

σ_{coh} = coherent scattering cross section

σ_{inc} = incoherent scattering cross section

σ_{abs} = absorption cross section

Table I contains the cross sections σ and scattering lengths b for Cs and Au as used in the present paper.

TABLE I

Cross sections and scattering lengths for Cs and Au.

	σ_{coh}^4 [10^{-24} cm 2]	σ_{inc}^4 [10^{-24} cm 2]	$\sigma_{\text{abs}} (\lambda = 0.692\text{\AA})$ [10^{-24} cm 2] 5	b^4 [10^{-12} cm]
Au	7.45	0.36 4	36.52	0.763
Cs	3.74	0.22 a	10.89	0.542

 a This value was obtained during the present work (see below).

Attention was drawn already by Oehme 6 and Huijben 7 on the deviation between the tabulated and the directly observed value of the incoherent scattering cross section for Cs. These authors assumed $\sigma_{\text{inc}}^{\text{Cs}} < 1.0$ barn and 0.095 barn, respectively, which deviate appreciably from the tabulated value according to Ref. 4. Therefore it was necessary to measure directly by a transmission method the linear attenuation μ . The Cesium specimen had the dimensions 10 mm thick and 15 mm high, the neutron beam had a cross section of 0.2×3 mm 2 . The coefficient of linear attenuation of the specimen μ^s can be calculated from the measured intensities:

$$\mu^s = -\frac{1}{X_s} \ln \frac{I_{s+c+f} - I_{\text{Cd}}}{I_{c+f} - I_{\text{Cd}}} \quad (4)$$

For a Vanadium rod measured at room temperature we obtain

$$\mu^v = -\frac{1}{X_v} \ln \frac{I_v - I_{\text{Cd}}}{I_0 - I_{\text{Cd}}} \quad (5)$$

with

X_s, X_v = thickness of the specimen and the Vanadium-rod, resp.

I_{s+c+f} = measured intensity behind the specimen + container + furnace

I_v = measured intensity behind the Vanadium (without container and furnace)

I_{Cd} = measured intensity behind a Cd-specimen

I_{c+f} = measured intensity behind the container + furnace

I_0 = measured intensity of the primary beam

By use of the Cd-specimen the influence of the high energy neutrons which in spite of monochromatisation are contained in the primary beam can be eliminated.

Table II contains the measured coefficients μ^{exp} for molten Cs at two temperatures and for a Vanadium-specimen. Furthermore Table II contains the linear coefficients of attenuation μ^{lit} as calculated according to Eq. (1) from the values in Table I. For this calculation however $\sigma_{\text{inc}}^{\text{Cs}}$ was taken as 4.6 barn as reported in literature.

TABLE II
Measured and calculated linear coefficients
of attenuation

	Temperature [°C]	μ^{exp} [cm ⁻¹]	μ^{lit} [cm ⁻¹]
	100	0.121	0.157
Cs	300	0.114	0.147
V	25	0.486	0.489

If the deviations of the linear coefficients of attenuation for Cs are based on mistakes in the tabulated incoherent scattering cross section, we obtain from μ^{exp}

$$\sigma_{\text{inc}}^{\text{Cs}} = 0.22 \text{ barn} \pm 0.05$$

Note added in proof:

L. Koester, Garching, drew our attention on a paper of H. Glättli *et al.*, *J. Phys.* **40**, 629 (1979) who obtained by a direct method $\sigma_{\text{inc}}^{\text{Cs}} = 0.21 \text{ barn} \pm 0.056$.

NORMALIZATION PROCEDURE

Having obtained from the measured intensities the intensity $I_{\text{corr}}(q)$ corrected for absorption as well as for scattering of furnace and container, we have to treat the incoherent and multiple scattering which are gathered together as background scattering. In the following we present a method for the direct determination of the structure factor $S(q)$ from I_{corr} by corresponding consideration of the background scattering intensity I_b . Since I_b is independent from q and since for $q \rightarrow \infty$ the structure factor reaches 1, we write

$$S(q) = \frac{I_{\text{corr}}(q) - I_b}{I_{\text{corr}}(\infty) - I_b} \quad (6)$$

From Eq. (6) we obtain

$$I_b = \frac{I_{\text{corr}}(0) - I_{\text{corr}}(\infty) \cdot S(0)}{1 - S(0)} \quad (7)$$

with

$$S(0) = \rho_0 k_B T K_T \quad (8)$$

k_B = Boltzmann's constant

T = absolute temperature

K_T = isothermal compressibility

$I_{\text{corr}}(0)$ is obtained by extrapolation of the corrected intensity for $q \rightarrow 0$.

$I_{\text{corr}}(\infty)$ is obtained by extrapolation of the corrected intensity for $q \rightarrow \infty$.

However, during the experiment one observes I_{corr} only up to a finite value q_{max} . By a variation of the method of Krogh-Moe⁷ we obtain

$$I_{\text{corr}}(\infty) = \frac{\int_0^{q_{\text{max}}} q^2 I_{\text{corr}}(q) dq - 2\pi^2 \rho_0 I_b}{(q_{\text{max}}^3/3) - 2\pi^2 \rho_0} \quad (9)$$

with

$$q_{\text{max}} = \text{maximum measured } q\text{-value}$$

Table III contains the parameters for the calculation of $S(0)$. The number density ρ_0 for Cs was taken from Ref. 8.

TABLE III
Measuring temperature, number density, compressibility, and structure factor $S(q = 0)$ for Au and for Cs

	Temperature [°C]	ρ_0 [atoms/Å ³]	$K_T \cdot 10^{12}$ [$\frac{\text{cm sec}^2}{\text{g}}$]	$S(0)$
Au	1100	0.0528 ⁹	1.23 ¹⁰	0.012
	100	0.00817	74.89 ¹¹	0.031
Cs	300	0.00765	91.81 ¹¹	0.056
	600	0.00687	138.85 ¹¹	0.115

EXPERIMENTAL RESULTS

Structure-factors

Figures 1a to c show the measured structure-factors obtained with molten Cs at 100°C, 300°C, and 600°C. In the q -region below 0.18 \AA^{-1} the structure factor was extrapolated to $S(0)$ calculated according to Eq. (8). No oscillations of $S(q)$ could be observed for q larger than 7 \AA^{-1} .

Figure 2 shows the run of $S(q)$ for molten Au at a temperature of 1100°C in the q -region from 0.18 \AA^{-1} up to 10 \AA^{-1} .

Table IV contains besides the characteristic data from Figure 1a to c and Figure 2 also data from other references.

The structure factor obtained from molten Cs at 100°C is in good accordance with that obtained by Huijben and van der Lugt¹² concerning the position q_1 and q_2 of the first and second maximum as well as the height $S(q_1)$ of the first maximum. The structure factor in Ref. 12 was obtained by X-ray diffraction. In that paper however, the structure factor $S(0)$ for $q = 0$ was 10% larger than that which follows from the thermodynamic data. The comparison of the present data obtained at 300°C and 600°C with

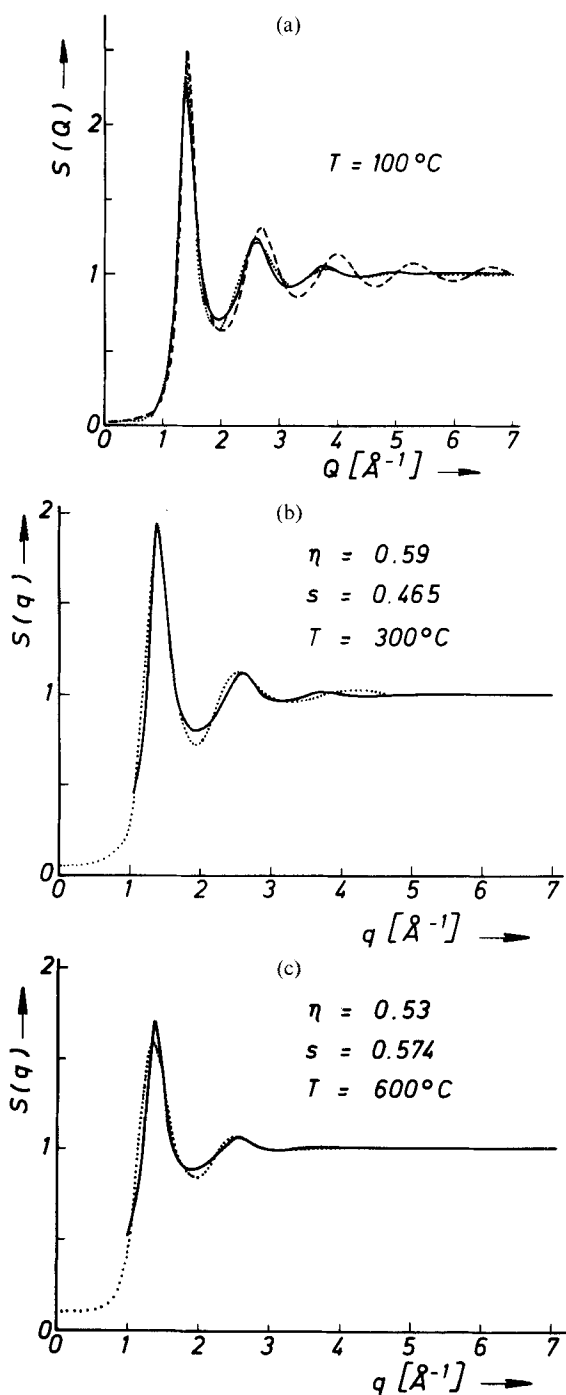


FIGURE 1 Structure factor of molten Cs experimental run, ——— hard sphere model according to Blétry, ······ hard sphere model according to Ashcroft and Lekner.

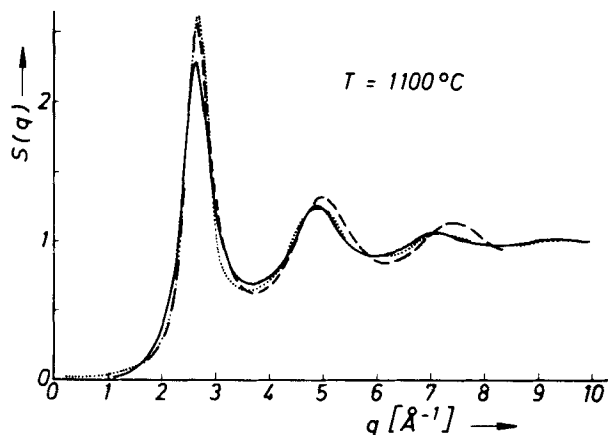


FIGURE 2 Structure factor of molten Au at 1100°C experimental run, ——— hard sphere model according to Blétry, - · - · - · hard sphere model according to Ashcroft and Lekner.

TABLE IV

Structural data of molten Cs and Au

	Temperature [°C]	q_1 [Å ⁻¹]	q_2 [Å ⁻¹]	$S(q_1)$	Reference
Cs	100	1.43	2.62	2.49	present paper
	300	1.40	2.57	1.89	present paper
	600	1.36	2.53	1.61	present paper
	100	1.43	2.63	2.55	¹²
	300	1.42	2.70	1.80	¹³
	579	1.37	2.76	1.70	¹³
Au	1100	2.7	4.92	2.61	present paper
	1100	2.7	4.95	2.51	¹⁴

those obtained by Gingrich and Heaton¹³ using neutron diffraction, confirms the shift of the first maximum to smaller q -values during rise of the temperature. There is a discrepancy concerning the position of the second maximum between Ref. 13 and the present paper.

PAIR CORRELATION FUNCTIONS

From the structure factor obtained according to Eq. (6) the pair correlation function $g(r) = \rho(r)/\rho_0$ can be calculated according to Eq. (10). $\rho(r)$ means the local number density in the distance r around a reference atom.

$$g(r) = 1 + \frac{1}{2\pi^2\rho_0 r} \int_0^\infty q(S(q) - 1)\sin(qr)dq \quad (10)$$

Figure 3 shows the pair correlation function of Cs and Figure 4 that of gold.

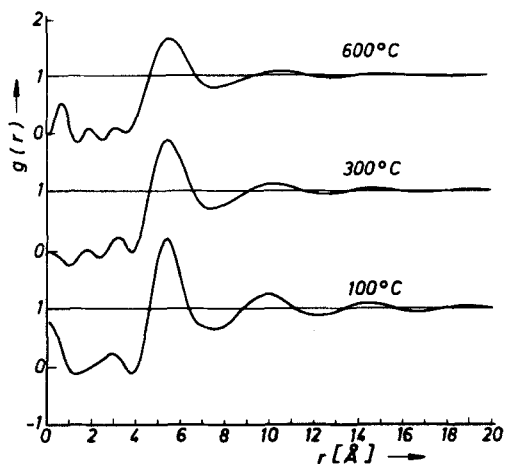


FIGURE 3 Pair correlation function of molten Cs.

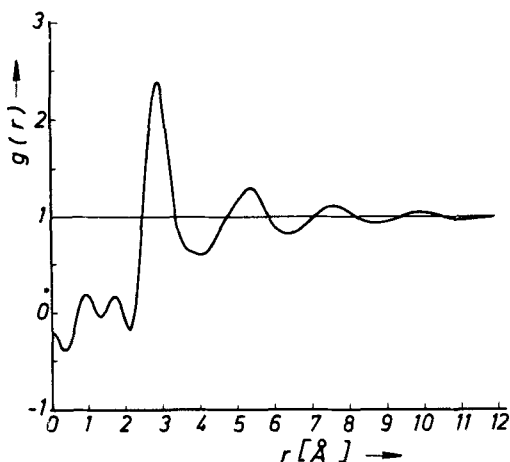


FIGURE 4 Pair correlation function of molten Au.

The oscillations at small r -values result from the finite integration length and have no physical meaning. It should be mentioned the occurrence of an additional maximum between the first and second main maximum in the pair correlation function obtained from a Cs-melt at 300°C in Ref. 13 whose existence could not be proved during the present work.

Table V contains the distances r^I of the first coordination sphere obtained from the pair correlation function $g(r)$ and the coordination number N^I as obtained for the first coordination sphere from the radial distribution function $4\pi r^2 g(r) \rho_0$. Thereby the method of symmetrical main maximum was used.

TABLE V

Radius r^j and coordination number N^j in molten Cs and Au

	Temperature [°C]	r^j [Å]	N^j [atoms]
Cs	100	5.33	10.9
	300	5.38	9.9
	600	5.43	10.3
Au	1100	2.85	9.0

DISCUSSION AND RESULTS

In this chapter structure factors according to the methods of Ashcroft and Lekner¹⁵ and of Blétry¹⁶ will be calculated and compared with the experimental structure factors.

As Ashcroft and Lekner showed using hard sphere potentials, the Percus-Yevick-approximation¹⁷ yields an analytical expression for the structure factor. The fitting of the Ashcroft-Lekner structure factor $S^{\text{AL}}(q)$ to experimental results is done by variation of the packing density η for which stands

$$\eta = \frac{\pi}{6} \rho_0 d^3 \quad (11)$$

Thus, using the experimental number density ρ_0 , by Eq. (11) also the atomic diameter d is fixed. The fit of the calculated $S^{\text{AL}}(q)$ -curves to the first main maxima obtained experimentally led to the η - and d -values given in Table VI. As can be seen from Figures 1a and 2, there are differences between the experimental and theoretical curves which become larger with growing q and which show that the oscillations of $S^{\text{AL}}(q)$ are less damped and shifted to larger q -values.

TABLE VI
Parameters for model calculations

	Temperature [°C]	$S^{\text{AL}}(q)^a$		$S^{\text{B}}(q)^b$		
		η	$d[\text{Å}]$	η	$d[\text{Å}]$	$s[\text{Å}]$
Au	1100	0.452	2.55	0.633	2.84	0.185
Cs	100	0.45	4.75	0.648	5.33	0.375

^a $S^{\text{AL}}(q)$: Structure factor according to Ashcroft and Lekner.

^b $S^{\text{B}}(q)$: Structure factor according to Blétry.

The model according to Blétry¹⁶ is based on a computer calculation in which 15812 hard spheres with diameter d_0 were used. By convenient boundary conditions a ball shape with packing density η_0 of the whole arrangement is maintained. From the distribution of the atomic distances follows the pair correlation function and from this by a Fourier Transform the structure factor S_{d_0, η_0} . For an arrangement with a hard sphere diameter d and packing density η the following formula stands for the calculation of the Blétry structure factor $S_{d, \eta}^B$:

$$S_{d, \eta}^B(q) = 1 + \frac{\eta}{\eta_0} e^{-s^2 q^2} \left[S_{d_0, \eta_0} \left(q \cdot \frac{d}{d_0} \right) - 1 \right] \quad (12)$$

with

$$s^2 = \frac{k_B \cdot T}{4\pi^2 m v^2} \quad (13)$$

m = atomic mass

v = atomic vibration frequency

T = temperature in K

S_{d_0, η_0} = structure factor following from the Blétry-model¹⁹ ($d_0 = 2 \text{ \AA}$;
 $\eta_0 = 0.5685$)

From Eq. (12) we recognize that Blétry has introduced a temperature-dependent factor which is deduced analogous to the Debye-Waller factor for solids in harmonic approach. The atomic oscillation frequency has according to Ref. 16 for metallic melts half the value of the Debye-frequency ν_D of the corresponding crystalline phase.¹⁸ The packing density η follows according to Eq. (11) from the mean number density ρ_0 determined experimentally and the hard sphere diameter d . The latter was adjusted for optimum fitting. The values for d and η which were used finally are given in Table VI. It should be noted that the d -values differ less than 1.5% from the corresponding Goldschmidt-diameters given in Ref. 20. A similar finding has been reported by Blétry.¹⁶

Furthermore these d -values are in good accordance with the radii of the first coordination sphere of Au ($T = 1100^\circ\text{C}$) and Cs ($T = 100^\circ\text{C}$) as obtained in the present work.

The structure factor $S^B(q)$ according to Blétry shows oscillations in the q -region below $3/d \text{ \AA}^{-1}$ which arise from deviations from the spherical shape of the whole arrangement. Therefore the comparison between experimental and calculated structure factors should only be done in the q -region with $q > 3/d$.

A good accordance between $S^B(q)$ and the experimental structure factor can especially be observed in the region of larger q 's by using the atomic vibration frequencies $\nu_{\text{Au}} = 2.07 \cdot 10^{12} \text{ sec}^{-1}$ and $\nu_{\text{Cs}} = 0.648 \cdot 10^{12} \text{ sec}^{-1}$.

A marked difference between $S^B(q)$ and the experimental result can be detected in the region of the first maximum in Figure 1a and 2, where $S^B(q)$ is smaller than the experimental result. A similar behaviour was already observed in Ref. 16 for Zn- and Rb-melts near the melting point and can be explained by the neglect of the long-range-part of the atomic potential in the calculation of Blétry.

Figures 1b and 1c show the $S^B(q)$ of molten Cs for 300°C and 600°C. These figures also contain the temperature dependent parameters η and s which are given by Eqs. (11) and (13) as well as the experimental $S(q)$. Here only the comparison with Blétry's model is represented, since at 100°C a better fit to the experimental data was achieved using this concept. In both cases there is rather good accordance between experimental and calculated structure factors for $q > 1 \text{ \AA}^{-1}$. The temperature-dependent shift of the main maximum cannot be reproduced by the model since this behaviour is based on anharmonic effects.

SUMMARY

Neutron diffraction experiments ($\lambda = 0.692 \text{ \AA}$) were done with molten Au and molten Cs. The experimental structure factors can be well described by a hard sphere model according to Blétry. Compared to the Ashcroft-Lekner procedure this model yields a better fit of between 100 and 600°C the high q range of $S(q)$ of Cs Molten Au (1100°C) and molten Cs (100°C) show rather the same packing density whereas in crystalline state Au is fcc and Cs bcc.

Acknowledgements

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