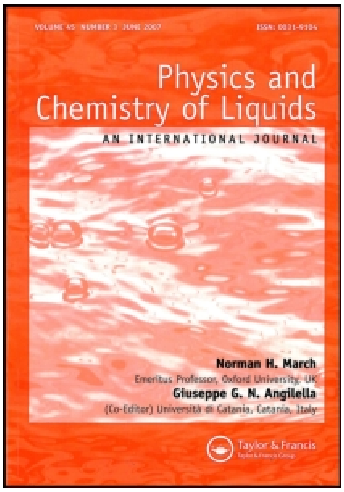

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Structure and Density of Gold-Cesium-Melts

IV. Density Measurements with Au-Cs-Melts

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INTRODUCTION

For the quantitative evaluation of neutron diffraction experiments and other physical measurements of molten metals and alloys the knowledge of the density is important. Furthermore the molar volume which is directly connected with the density represents itself a physical quantity which is essential for the discussion of structural results.

Different methods for the experimental determination of the density of melts were discussed in Refs. 1, 2. In the present paper the density of Au-Cs-melts was determined by the method of γ-absorption which has the advantage to need only small specimens and furthermore allows the specimen to be enclosed in a vacuum tight container during the measurement.

EXPERIMENTAL PRINCIPLE

The density measurement by means of γ-absorption is based on the attenuation law for monochromatic radiation:

$$I(X) = I_0 \exp(-\mu X) \tag{1}$$

$\mu = \mu(E, Z)$ means the linear attenuation coefficient which depends on photon energy E and the atomic number Z. X means the thickness of the absorber. I_0 and I are the primary intensity and the intensity measured

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behind the specimen in the direction of the primary beam. For a specimen s inside a container c we obtain at a given temperature for the empty and for the filled container the following relationships:

$$I_c = I_0 \exp(-2\mu_c X_c) \tag{2}$$

$$I_s = I_0 \exp(-2\mu_c X_c) \exp(-\mu_s X_s) \tag{3}$$

with

μ_c = linear attenuation coefficient of the container material
μ_s = linear attenuation coefficient of the specimen
X_c = thickness of the container material transversed by the beam
X_s = thickness of the specimen

Replacing μ_s by the mass attenuation coefficient $U_s = \mu_s(T)/D_s(T)$, with D_s being the density of the specimen, we obtain:

$$\left(\frac{I_s}{I_c}\right)_T = \exp[-U_s D_{s,T} X_s^0(1 + \tau \cdot T)] \tag{4}$$

with

τ = linear coefficient of expansion of the container material

In Eq. (4) also the temperature-dependent change of the specimen thickness which is caused by the expansion of the container is taken into account.

To replace the specimen thickness X_s^0, the intensity is also measured for a reference specimen with known density in a container with the same dimensions at the temperature T_0. In this case Eq. (4) will be written as

$$\left(\frac{I_r}{I_c}\right)_{T_0} = \exp[-U_r D_{r,T_0} X_s^0(1 + \pi T_0)] \tag{5}$$

The index r means the corresponding quantity of the reference specimen. The Eqs. (4) and (5) yield

$$D_{s,T} = \frac{U_r}{U_s} D_{r,T_0} \frac{(1 + \tau T_0)}{(1 + \tau T)} \frac{\ln(I_s/I_c)_T}{\ln(I_r/I_c)_{T_0}} \tag{6}$$

Equation (6) only contains quantities known from literature and the intensities to be measured experimentally.

EXPERIMENTALS

Specimen preparation and γ-source

Equation (6) is valid for flat specimens. Therefore plane parallel containers made from molybdenum were used as shown in Figure 1 (longitudinal section). The windows were made from molybdenum foil (0.5 mm) which

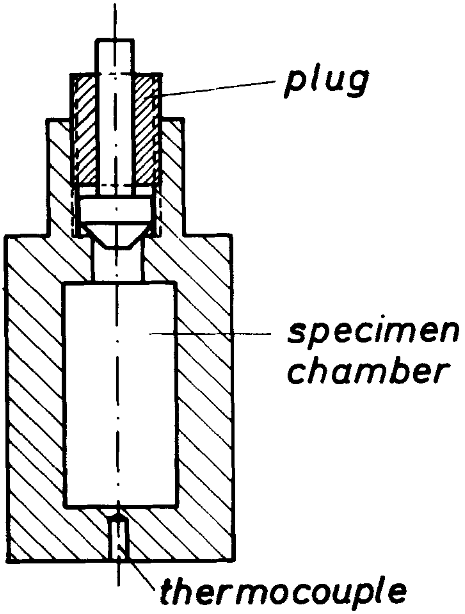

FIGURE 1 Specimen container for density measurements.

were connected vacuum tight with the frame by diffusion-welding.[3] The containers were filled with Au and Cs within a glove box containing ultrapure Ar. Then they were closed by means of a molybdenum screw, which presses a niobium cone versus the sharp edge of a cylindrical hole. The dimensions of the specimen are $B \times T \times H = 10 \times 10 \times 12\,\mathrm{mm}^3$. For each specimen a new specimen container had to be used. Therefore it was necessary to keep the thickness of the container frames within 0.1 % which was performed by polishing and lapping.

The choice of the γ-source, i.e. the photon energy is influenced by the specimen thickness. The relative error $\Delta D_s/D_s$ during the determination of the specimen density, as far as it is determined by the counting statistics, can be calculated according to Ref. 4 as follows:

$$\frac{\Delta D_s}{D_s} \simeq \frac{2}{U_s D_s X_s} \cdot \frac{\Delta I}{I} \tag{7}$$

For an expected relative error $\Delta D_s/D_s$ of 1 ‰ which mainly will be influenced by the counting statistics $\Delta I/I$ which also shall be 1 ‰ we obtain

$$U_s D_s X_s = 2 \tag{8}$$

Thus with $X_s = 1$ cm and $D_s = 7$ g/cm^3, which is the density of solid state AuCs,[5] the mass attenuation coefficient should be $U_s = 0.3$ cm^2/g. This condition is satisfied using the 0.31 MeV γ-radiation of Ir^{192}.[6,7] The activity of the source used during the measurements was 0.5 to 1 Curie.

EXPERIMENTAL DETAILS

Figure 2 shows the experimental arrangement as well as the electric components in a schematic diagram. The Ir^{192} source has a diameter of 2 mm and is contained in an aluminum capsule surrounded by a lead-shield. The primary beam is collimated. The specimen is fixed within a quartz tube of wall-thickness 5 mm in a reproducible way and can be heated in vacuum up to 950°C. The discrimination of the 0.31 MeV-line from the whole Ir^{192}-spectrum is done by a multi-channel-analyzer.

Before each series of measurements the corresponding melt was kept at least eight hours at 600°C to assure a homogeneous mixing of the specimen. This was confirmed by the fact that the check of the pulse rates yielded no variation at least during further two hours. During the following stepwise increase of temperature by 30°C the melts immediately assumed equilibrium state and thus the measurements could be done instantly. The results were checked by performing measurements at the corresponding temperature during the cooling down of the specimen. The measuring period was 200 s or 500 s. The accumulated pulse number amounted 5.10^5 up to 8.10^5.

According to Eq. (6) the intensity of the reference specimen is needed for the density calculation. We used a Cesium-specimen, the corresponding

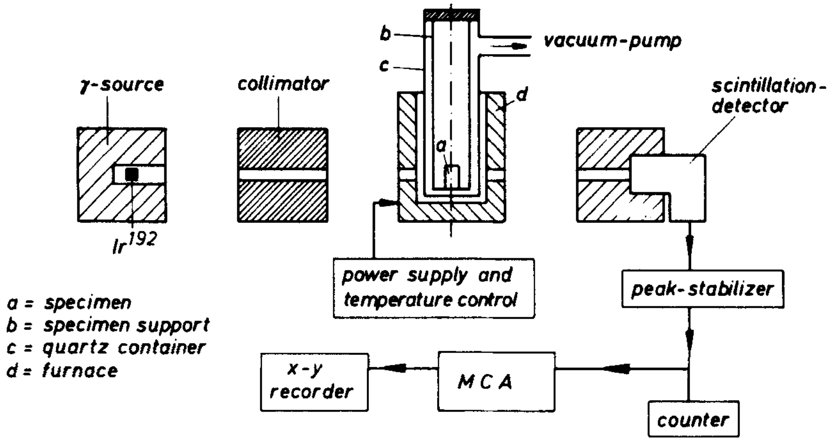

FIGURE 2 Density measurement: Schematic diagram of the experimental arrangement.

measurements were done immediately after each complete temperature run. To check the efficiency of the measuring method, the absolute density of Cesium as well as its temperature dependency was determined and compared with literature. For this purpose as a reference liquid mercury was used, the density of which is known very precisely.[8] Table I contains the mass attenuation coefficient of the elements Cs, Au, and Hg, which were taken from tables or interpolated from the data of neighboured elements (see Refs. 9, 10).

TABLE I

Mass attenuation coefficients of Cs, Au, and Hg for $E = 0.31$ MeV

Element	Cs	Au	Hg
U[cm^2/g]	0.177	0.349	0.358

The coefficients $U_{\mathrm{Au-Cs}}$ for the molten Au-Cs-alloys are calculated from the corresponding coefficients for the molten elements according to the following Eq. (9):

$$U_{\mathrm{Au-Cs}} = g_{\mathrm{Cs}} U_{\mathrm{Cs}} + g_{\mathrm{Au}} U_{\mathrm{Au}} \tag{9}$$

g_i are the weight fractions

$$\left(\sum_i g_i = 1\right).$$

The mass attenuation coefficients contain an error of approximately 1% and therefore are the largest contribution to the total error of the density determination. Further sources of error are given by deviations of the specimen thickness, by the statistical variation of the counting rate and finally by the dead time of the scintillation counter and the counting electronics. The total error of the density was estimated to be ±1.5%.

RESULTS AND DISCUSSION

Figure 3 shows the density of molten Cs as determined during the present work for temperatures between 50°C and 280°C. The temperature dependency in this region is represented by a linear relationship:

$$D(T) = D_0 - \frac{\Delta D}{\Delta T} T \tag{10}$$

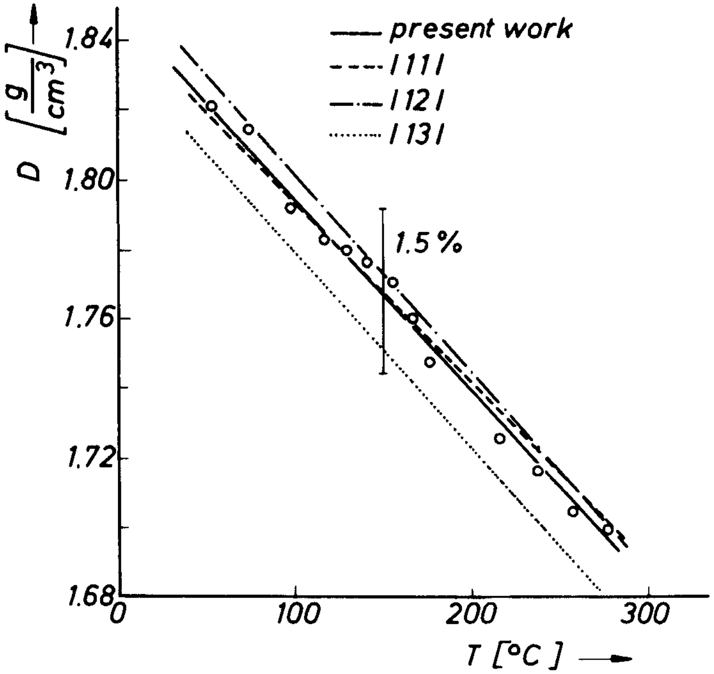

FIGURE 3 Molten Cs: Density D versus temperature T ○○○○○ = measured data.

The straight line calculated by the least squares method is drawn as full line in Figure 3 which also contains the densities from Ref. 11, 12, and 13. We observe good accordance within the limits of error.

Figure 4 shows the results of density measurements with Au-Cs-melts. The parameters D_0 and $\Delta D/\Delta T$ from Eq. (10) are given in Table II for all melts investigated. Using these parameters with Eq. (10) it is to pay attention to the fact that the temperature must be given in °C.

TABLE II

Au-Cs-melts: Parameters determined experimentally

Cs-concentration [at%]	100	80	75	70	60	50
D_0 [g/cm^3]	1.854	2.934	3.401	3.816	5.177	7.146
$\frac{\Delta D}{\Delta T}\cdot 10^4$ [g/cm^3 grd]	5.7	6.6	7.1	8.2	12.2	17.1

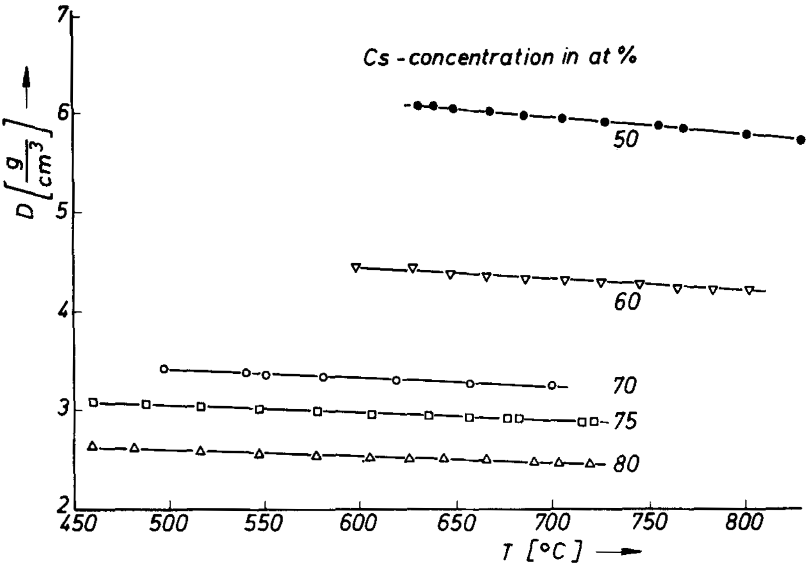

FIGURE 4 Au-Cs-melts: Density versus temperature.

For the following discussion it is useful to use the molar volumina. For the molar volume V_M of a multicomponent melt stands

$$V_M = \frac{\sum_i c_i M_i}{D} \tag{11}$$

with

D = density of the melt
c_i = atomic fraction of component i
M_i = atomic weight of component i

For an ideal binary melt the molar volume can be calculated as follows:

$$V_M^{\text{ideal}} = c_1 \frac{M_1}{D_1} + c_2 \frac{M_2}{D_2} \tag{12}$$

D_i = density of the unalloyed component i.

The molar excess volume ΔV_M is given by

$$\Delta V_M = V_M - V_M^{\text{ideal}} \tag{13}$$

Figure 5 shows for Au-Cs-melts at 600°C the plot of V_M, V_M^{ideal}, and ΔV_M vs. Au-concentration. The molar volume of the Au-melt whose melting point is higher than 600°C was extrapolated from the data given in Ref. 15. The dashed line indicates the liquidus temperature being higher than 600°C

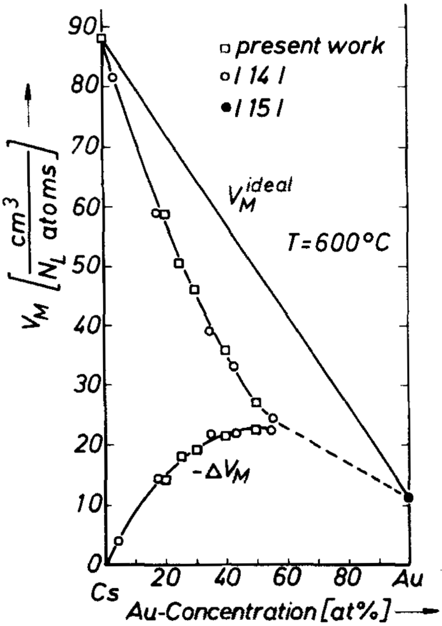

FIGURE 5 Au-Cs-melts: Molar volume V_M and excess volume ΔV_M.

in the corresponding region. The results of Kempf[14] who recently measured by an indirect archimedian method the density also are shown in Figure 5. The magnitude of the excess volume is maximum for the melt with 50 at% and amounts to 45.5% of V_M^{ideal}. At this point it must be mentioned that normally the deviation of the molar volume from the ideal volume for binary melts with metallic components never exceeds 3%.

In the last section we will compare the molar volume of Au-Cs-melts with that of molten salts, which was given in Ref. [16] as follows:

$$V_M^{\text{salt}} = 4N_L[(r^+)^3 + (r^-)^3] \qquad (14)$$

with

N_L = Avogadro's number
r^+, r^- = ionic radii

If we use the ionic radii deduced in Ref. 17 for Au^-- and Cs^+-ions we obtain the figures given in Table III together with those obtained experimentally at 600°C for the molten compound AuCs and for some molten salts.[18]

According to Table III for molten salts with the composition NaCl, KCl, RbCl, and CsCl we obtain $V_M^{\text{salt}} < V_M^{\text{exp}}$. This discrepancy is explained by

TABLE III

Molar volume at the melting point [cm^3/mol]

Substance	LiCl	NaCl	KCl	RbCl	CsCl	CsAu
$V_M^{exp\,a}$	14.1	18.8	24.4	26.9	30.1	26.9
$V_M^{salt\,b}$	14.8	17.12	19.95	22.0	25.9	27.7

[a] V_M^{exp} calculated from experimental densities.
[b] V_M^{salt} calculated from Eq. (14) from ionic radii.

holes in the melts whose volume was disregarded in Eq. (14). For AuCs and LiCl good accordance can be stated between the molar volume calculated from experimental densities and that calculated according to Eq. (14).

SUMMARY

By means of γ-absorption the density of molten Au-Cs-alloys was determined. The molten compound AuCs shows large volume contraction which reflects the molten salt like behaviour of AuCs.

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