Density and thermal expansion of silver in the solid and liquid states

R N Abdullaev, R A Khairulin and S V Stankus
Kutateladze Institute of Thermophysics SB RAS, 630090, Novosibirsk, Russia
E-mail: abdullaev.rasul88@gmail.com

Abstract. Density and thermal expansion of pure silver are investigated using a gamma-ray attenuation technique in the temperature range of 293–1631 K of solid and liquid states. The relative density change of silver during the solid–melt phase transition is directly measured. The approximation dependences for the density are constructed and the data of this work are compared with the results of other authors. Tables of temperature dependences of the volumetric properties of silver are developed over the entire measurement interval and their errors are estimated.

1. Introduction
Silver is a noble metal widely used in industry both in its pure form and as a component of various alloys and chemical compounds. Volumetric properties of silver have been studied for a long time and in a large number of works [1–15]. However, the results of these measurements do not agree well with each other. This applies particularly to the liquid state. Thus, the scatter of published data on the melt density at the melting temperature reaches about 4% [2, 5], and the results of experimental studies of the volumetric thermal expansion coefficient (VTEC) of liquid silver differ from each other more than two times [2, 3]. Density is one of the most important characteristics of a substance from both a fundamental and a practical point of view. In this connection, the aim of the present work is an experimental study of the density and thermal expansion of silver in the temperature range of 293–1631 K of solid and liquid states.

2. Experimental technique
Measurement of the thermal expansion of solid and liquid silver and a change in its density during melting–crystallization was carried out by using gamma-ray attenuation technique (gamma-method). The experimental setup and the measurement procedure were described in detail in [16, 17]. The cesium-137 isotope was used as a radiation source. The calculation of the relative volumetric changes in the sample during its heating or cooling was carried out from the experimental temperature dependences of the intensity of radiation transmitted through the sample. The construction of a polytherm of silver density was performed by a relative version of the gamma-method using the measured values of VTEC in the solid and liquid states, the relative density change at the phase transition, and density at room temperature \( \rho_r = 10503.8 \text{ kg m}^{-3} \), calculated from data [18] on lattice parameters with an error of less than 0.004%.

The test sample having a mass of about 197 g was prepared from silver with a purity of 99.99 mass%, which was previously degassed by melting in vacuum and holding for about an hour at a pressure of less than 5 mPa and a temperature of 1300 K. The temperature was measured by
tungsten-rhenium thermocouples immersed in the sample in protective sleeves of beryllium oxide. Before the experiments, the outer surface of the thermowells was coated with a layer of graphite. A verification of the thermocouples calibration by the solidification points of five pure metals has shown that the error in determining the temperature in the range of 293–1600 K did not exceed three degrees. All experiments were carried out in an atmosphere of pure argon, and cylindrical crucibles made of graphite with an inner diameter of 27 mm were used as measuring cells. Graphite was chosen as the material for the crucible, since, according to [19], no more than 0.0002 at.% of carbon dissolves in the silver melt at 1630 K. To minimize the error in measuring the thermal expansion coefficient of silver, the thermal expansion of graphite was investigated with high accuracy by dilatometer method (on the Netsch DIL-402C setup) with a sample made from the same bar as the measuring crucible.

3. Results and discussion

Figure 1 presents the raw data on the density of the solid and liquid silver. The temperature dependence of the density of silver in the solid phase from 293 K to the melting temperature $T_f = 1234.93$ K (reference point according to ITS-90) has no peculiarities and is well approximated by quadratic polynomial:

$$\rho_c(T) = 10503.8 - 0.6453 \cdot (T - 293.15) - 6.94 \cdot 10^{-5} \cdot (T - 293.15)^2, \text{ kg m}^{-3}$$

(1)

The density of solid silver at the melting point $\rho_f(T_f) = 9834.5$ kg m$^{-3}$ calculated from (1) differs by no more than 0.03% from the value calculated using $\rho_s$ and the reference data on VTEC [1].

![Figure 1. Temperature dependence of the density of silver in solid and liquid states, including the region of melting–crystallization. Points are experimental data. Lines are approximation dependences.](image)

The weighted mean values of the measured relative density change $\delta \rho_f$ during the solid–liquid phase transition and the VTEC of the melt $\beta_m$, at temperature $T_f$ are $\delta \rho_f = (5.16 \pm 0.14)\%$ and $\beta_m(T_f) =$
10.67±0.20 K\(^{-1}\), respectively. The values of the VTEC of the melt at the melting point and the relative density change during melting–crystallization in several heating-cooling cycles are reproduced within random measurement errors. The absence of gas inclusions at the crucible – melt interface and shrinkage defects during crystallization is controlled by scanning the sample with gamma rays. The obtained \(\delta \rho_i\) value within the measurement error coincides with that recommended in the review paper [15]. The experimental data on the density of the liquid sample are approximated by linear temperature dependence:

\[
\rho_n(T) = 9327.1 - 0.9956(T - 1234.93), \text{ kg m}^{-3}
\]  

(2)

Table 1 shows the smoothed values of the density \(\rho\) and VTEC \(\beta\) of silver in the solid and liquid states, consistent with each other.

| State | \(T\) (K) | \(\rho\) (kg m\(^{-3}\)) | \(\beta\) (10\(^{-5}\) K\(^{-1}\)) | Error (%) |
|-------|-----------|-----------------|-----------------|-----------|
|       |           | \(\rho\)       | \(\beta\)       | \(\delta \rho\) | \(\delta \beta\) |
| Solid | 293.15    | 10503.8         | 6.14            | 0.004     | 4.8         |
|       | 300       | 10499.4         | 6.16            | 0.006     | 4.8         |
|       | 400       | 10434.0         | 6.33            | 0.03      | 3.7         |
|       | 500       | 10367.3         | 6.50            | 0.06      | 2.8         |
|       | 600       | 10299.2         | 6.68            | 0.07      | 2.0         |
|       | 700       | 10229.8         | 6.86            | 0.09      | 1.6         |
|       | 800       | 10158.9         | 7.04            | 0.10      | 1.8         |
|       | 900       | 10086.6         | 7.23            | 0.11      | 2.4         |
|       | 1000      | 10013.0         | 7.42            | 0.13      | 3.1         |
|       | 1100      | 9938.0          | 7.62            | 0.16      | 3.9         |
|       | 1200      | 9861.5          | 7.82            | 0.19      | 4.8         |
|       | \(T_f = 1234.93\) | 9834.5 | 7.89 | 0.21 | 5.1 |
| Liquid | \(T_f = 1234.93\) | 9327.1 | 10.67 | 0.25 | 1.9 |
|        | 1300      | 9262.3          | 10.75           | 0.26      | 1.9         |
|        | 1400      | 9162.7          | 10.87           | 0.29      | 1.9         |
|        | 1500      | 9063.2          | 10.98           | 0.31      | 1.9         |
|        | 1600      | 8963.6          | 11.11           | 0.34      | 1.9         |
|        | 1631      | 8932.7          | 11.15           | 0.34      | 1.9         |

Table 2 compares the results of this work for liquid silver at the melting point with the data of other authors. It can be seen that the results of measurements [8–14] performed by the Archimedean method (A), the maximum bubble pressure technique (MBP) and gamma-method (GM) are in the best agreement with our results both in density and in VTEC (within the total measurement errors). The highest values of \(\delta \rho_n(T_f)\) were obtained in [2–7], where the measurements were mainly performed by various versions of the drop method (sessile drop method SD and electromagnetic levitation method EML). This can be explained by the errors in measuring the temperature of the samples accompanying these methods. Note that the above A, MBP, SD and EML techniques, in contrast to the GM used in...
[13] and present work, cannot measure relative volume changes without using data on the density, mass, and geometric dimensions of the sample. This inevitably leads to a number of systematic errors in determining the values of the VTEC [17]. However, the measurements of the VTEC were performed in [13] with larger uncertainties (±4.8%) than in the present work. This suggests that the results of this study on the volume coefficient of thermal expansion of liquid silver are the most reliable in the temperature range of 1234.93–1631 K and can be recommended as reference data.

Table 2. Comparison of the results of this work with literature data (in order of decreasing deviation of the VTEC from our data). $\delta \rho_m(T_f)$ and $\delta \beta_m(T_f)$ are relative deviations of literature data on $\rho_m(T_f)$ and $\beta_m(T_f)$ from the results of this work.

| Reference | Year | Method | Temperature interval (K) | Purity (wt.%) | $\delta \rho_m(T_f)$ | $\delta \beta_m(T_f)$ |
|-----------|------|--------|--------------------------|--------------|---------------------|---------------------|
| [2]       | 2015 | SD, MBP| 1273–1573                | 99.9         | 2.69                | 38.0                |
| [3]       | 1929 | A      | 1273–1473                | —            | -0.97               | -34.1               |
| [4]       | 2005 | SD     | 1273–1523                | 99.995       | -0.25               | -28.5               |
| [5]       | 2006 | EML    | 1250–1380                | —            | -1.90               | -24.2               |
| [6]       | 1989 | SD     | 1234–1873                | 99.99        | -0.18               | -21.5               |
| [7]       | 2010 | SD     | 1273–1573                | 99.999       | -0.40               | 18.5                |
| [8]       | 1962 | A      | 1234–2450                | 99.95        | 0.20                | -9.1                |
| [9]       | 2003 | MBP    | 1273–1473                | 99.995       | 0.20                | -8.7                |
| [10]      | 1969 | MBP    | 1273–1473                | —            | 0.35                | 8.1                 |
| [11]      | 1964 | MBP    | 1234–1673                | —            | 0.11                | 5.4                 |
| [12]      | 1972 | A      | 1234–1773                | —            | -0.08               | -2.5                |
| [13]      | 1992 | GM     | 1235–2300                | 99.99        | -0.13               | -2.1                |
| [14]      | 1975 | A      | 1234–1400                | 99.999       | 0.06                | -1.6                |

Conclusion
New experimental data on the density and thermal expansion coefficients of pure silver in solid and liquid states have been obtained. Relative density change during the solid–melt phase transition has been directly measured. Good agreement between the obtained results and the most reliable literature data have been shown.

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