Volumetric properties of iron in the solid and liquid states

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Abstract. Density and thermal expansion of pure iron are investigated using a gamma-ray attenuation technique in the temperature range of 1020–2090 K of solid and liquid states. The relative density changes of iron during allotropic transformations and solid – melt phase transition are directly measured. The density of iron at room temperature is measured by the Archimedean method. The temperature dependence of the density of iron in the temperature range of 130–2090 K was constructed using the results of this work and a previous study of the thermal expansion of the α-phase. The data of this work are compared with the results of other authors.

1. Introduction
Iron is one of the most abundant metals on Earth and widely used in industry. In the solid state, iron is a ferromagnet and exists in three crystalline modifications at atmospheric pressure: α-Fe phase with body-centered cubic lattice (BCC) stable up to 1185 K, γ-Fe phase with a face-centered lattice cubic (FCC), which is stable in the range of 1185–1667 K, and δ-Fe phase with BCC lattice, which is stable up to melting temperature of 1811 K [1]. The volumetric properties of iron have been studied for a long time in a large number of works [1–20]. However, these measurement results are in poor agreement with each other. This is especially true for structural transformation regions, melting-crystallization region, high-temperature solid δ-Fe phase and liquid state. For example, the scatter of published data on the melt density at the melting temperature reaches about 3.5% [3, 15], and the results of experimental studies of the volume thermal expansion coefficient (VTEC) of liquid iron differ by more than two times [4, 13]. Density is one of the most important characteristics of a substance from both a practical and a fundamental point of view. It is determined by the structure of short-range order and the nature of interatomic interaction. Also it is directly related to volume, which is one of the main thermodynamic parameters of the state. Thus, the aim of the present work is an experimental study of the thermal expansion and density of pure iron in the temperature range of 1020–2090 K of solid and liquid states.

2. Experimental technique
Measurements of the relative changes in the density of iron during its heating or cooling were carried out by gamma-ray attenuation technique (gamma-method). The experimental setup and the measurement procedure are described in detail in [21, 22].

Samples for density and thermal expansion measurements were made of carbonyl refined iron produced by Sintez-CIP Ltd. with a purity of no worse than 99.98 mass%. Portions of iron were melted in crucibles from beryllium oxide and kept for about an hour in high vacuum. A sample weighing 158 g for gamma experiments was formed from the obtained degassed ingots. The absence of gas inclusions at the crucible – melt interface was controlled by scanning the sample with gamma rays. A sample for measuring density at room temperature was cut from the defect-free part of the obtained ingot after a
series of measurements on a gamma-densitometer. Earlier, part of the authors of this work used the dilatometric method to study the thermal expansion of α-Fe [19] in the range of 130–1180 K using a sample also cut from this ingot. The density $\rho_r$ of the iron sample at room temperature $T_r = 293.15$ K was measured by the Archimedean method. Distilled deaerated water was used as a reference liquid. The relative error in determining $\rho_r$ did not exceed 0.05%.

The temperature dependence of the density of α-Fe from 130 K to the transition temperature $T_{tr}$ between the α-Fe and γ-Fe phases was reconstructed using $\rho_r$ and data [19] on the relative expansion of iron. The calculation of the density of iron in the solid state $\rho_c$ (γ-Fe and δ-Fe phases) from the primary data of gamma experiments was carried out according to the formula:

$$\rho_c(T) = \rho_a(T_{tr}) \left\{ \frac{\ln[J_0(T)/J(T)]}{\ln[J_0(T_{tr})/J_a(T_{tr})]} \right\}^{3/2}$$  \hspace{1cm} (1)

Here $J(T)$, $J_a(T)$ are the intensities of radiation after passage through the measuring cell with and without the sample, respectively, $T$ is a temperature, subscript $a$ indicates α-Fe phase of iron. The melt density $\rho_m$ was calculated using the formula:

$$\rho_m(T) = \rho_m(T_i) \left\{ \frac{\ln[J_0(T_i)/J(T)]}{\ln[J_0(T_i)/J(T_i)]} \right\} \frac{1 + \alpha_g(T_i)(T_i - T)}{1 + \alpha_g(T)(T - T_i)}$$  \hspace{1cm} (2)

In the formula (2) $T_i$ is a melting temperature, $\alpha_g$ is the mean linear thermal expansion coefficient (MLTEC) of the crucible material. Relative density changes $\delta \rho$ during polymorphic transformations and melting-crystallization, as well as the volume thermal expansion coefficient $\beta$ were determined from the relative change in intensity $J$:

$$\delta \rho = \frac{\rho^-(T_i) - \rho^+(T_i)}{\rho^+(T_i)}, \quad \beta = -\frac{1}{\rho(T)} \left( \frac{\partial \rho(T)}{\partial T} \right)_p$$  \hspace{1cm} (3)

In the formula (3), the indices “−” and “+” relate the density to the high-temperature and low-temperature phases of iron, respectively, with respect to the transition temperature $T_i$. It can be seen from relations (1)–(3) that $\delta \rho$ and $\beta$ of the sample determined by the gamma method do not depend on the absolute value of its density and are calculated from the measured values of the radiation intensities and MLTEC of the crucible material.

The temperature of the sample was measured by tungsten-rhenium thermocouples immersed in the sample in protective sleeves of beryllium oxide. The thermocouple calibration was checked against the crystallization points of five pure metals. The deviations of the measured solidification temperatures from reference data did not exceed 3 K in the range of 293–2100 K. All experiments were carried out in a pure argon atmosphere, and cylindrical beryllium oxide crucibles with an inner diameter of 29 mm were used as measuring cells. The thermal expansion of the crucible material was studied earlier [23] with high accuracy, which made it possible to minimize the errors in measuring the thermal expansion coefficient of iron in the present work.

3. Results and discussion

The value of iron density $\rho_r$ at room temperature 293.15 K is found to be 7871.7±3.9 kg m$^{-3}$. The density of Fe calculated near $T_i$ from the literature data on the crystal lattice parameters [24] exceeds $\rho_r$ by only 0.035%.

The measured values of the VTEC of iron and its relative density changes on allotrophic transformations and melting in several heating-cooling cycles of the sample were reproduced within random measurement errors. Table 1 shows the temperatures of the iron phase transitions determined in this
work, as well as the weighted mean values of the measured relative density changes $\delta\rho$ on the corresponding transitions and VTEC of liquid and solid phases at the corresponding temperatures.

Table 1. Relative density changes of iron on the first-order phase transitions.

| Transition          | Temperature (K) | $\delta\rho$ (%) | $\beta \times 10^5$ K$^{-1}$ |
|---------------------|-----------------|------------------|------------------------------|
| $\alpha$-Fe $\rightarrow$ $\gamma$-Fe | 1181.4          | -1.39±0.20       | 6.77±0.34 ($\gamma$-Fe)     |
| $\gamma$-Fe $\rightarrow$ $\delta$-Fe | 1668.3          | 0.40±0.15        | 7.01±0.35 ($\gamma$-Fe)     |
| $\delta$-Fe $\rightarrow$ melt       | 1811.0          | 3.39±0.12        | 6.87±1.13 ($\delta$-Fe)     |
|                     |                 |                  | 8.66±0.22 (melt)             |

The value of $\delta\rho$ during melting-crystallization of iron obtained in the present work within the limits of measurement errors coincides with that recommended in the review paper [20]. The temperature dependence $\rho_0(T)$ was reconstructed using $\rho_r$ and data on the relative expansion of $\alpha$-Fe [19]. The value of $\alpha$-Fe density at the transition temperature $T_{\text{av}}$ is $\rho_0(T_{\text{av}}) = 7564.2\pm5.3$ kg m$^{-3}$. This value was used as a reference for constructing a density polytherm based on the results of gamma-experiments. Figure 1 shows the primary experimental data on the density of iron in the temperature range of 1020–2090 K.

Figure 1. Temperature dependence of the density of iron in solid and liquid states, including the regions of phase transitions.

The experimental data on the density for each phase were approximated by the least square method with linear temperature dependence:

$$\rho(T) = A - B(T - T_0)$$  \hspace{1cm} (4)
The coefficients of polynomial (4) are given in Table 2.

Table 2. Coefficients of the polynomial (4).

| Phase | $T_0$ (K) | $A$ (kg m$^{-3}$) | $B$ (kg m$^{-3}$ K$^{-1}$) |
|-------|-----------|------------------|---------------------------|
| $\gamma$-Fe | 1181.4 | 7669.3 | 0.5195 |
| $\delta$-Fe | 1668.3 | 7386.7 | 0.5023 |
| melt | 1811.0 | 7067.1 | 0.6119 |

Table 3 shows the smoothed temperature dependences of $\rho$ and $\beta$ of iron in the solid and liquid states, consistent with each other and with the results of [19], where, in particular, the vicinity of the Curie temperature $T_C$ was studied in detail.

Table 3. Volumetric properties of iron in the solid and liquid states.

| State | $T$ (K) | $\rho$ (kg m$^{-3}$) | $\beta$ ($10^{-5}$ K$^{-1}$) | Error (%) |
|-------|---------|----------------------|-------------------------------|-----------|

| $\alpha$-Fe | | | | |
|-------------|---------|----------------------|-------------------------------|-----------|
| $T_C = 1042.7$ | 7611 | 4.03 | 0.06 | 1.7 |
| 1045 | 7611 | 4.24 | 0.06 | 1.4 |
| 1050 | 7609 | 4.30 | 0.06 | 1.2 |
| 1100 | 7592 | 4.46 | 0.06 | 0.8 |

| $\gamma$-Fe | | | | |
|-------------|---------|----------------------|-------------------------------|-----------|
| $T_\alpha = 1181.4$ | 7564 | 4.63 | 0.07 | 0.8 |
| $T_\alpha = 1181.4$ | 7669 | 6.77 | 0.21 | 5.0 |
| 1200 | 7660 | 6.78 | 0.22 | 5.0 |
| 1300 | 7608 | 6.83 | 0.25 | 5.0 |
| 1400 | 7556 | 6.88 | 0.29 | 5.0 |
| 1500 | 7504 | 6.92 | 0.33 | 5.0 |
| 1600 | 7452 | 6.97 | 0.36 | 5.0 |

| $\delta$-Fe | | | | |
|-------------|---------|----------------------|-------------------------------|-----------|
| $T_\gamma = 1668.3$ | 7416 | 7.01 | 0.39 | 5.0 |
| $T_\gamma = 1668.3$ | 7387 | 6.80 | 0.42 | 16.5 |
| 1700 | 7371 | 6.81 | 0.45 | 16.5 |
| 1800 | 7321 | 6.86 | 0.57 | 16.5 |
| $T_\gamma = 1811.0$ | 7315 | 6.87 | 0.58 | 16.5 |
Table 4 compares the results of this work for liquid iron at the melting point with the data of other authors. It can be seen that the best agreement between the data on the volume thermal expansion coefficient of the molten iron is demonstrated by studies performed using the gamma-method (GM). The data on VTEC obtained by more traditional methods (the Archimedean method A, the maximum bubble pressure technique MBP, pycnometric method P, sessile drop method SD and electromagnetic levitation method EML) show a significantly larger spread. This feature should not be surprising, since the A, MBP, P, SD and EML techniques, unlike the gamma-method used in this work, are not able to measure relative volume changes without using data on the density, mass, and geometric dimensions of the sample, which inevitably involves a number of systematic errors in determining the values of the VTEC [22]. The coefficient \( \beta_m(T_f) \) calculated from the temperature dependence of the density of liquid iron (R) recommended in [8] also deviates significantly from the data of this work. This can be explained by the fact that the authors of [8] neglect the results of a number of studies performed by the gamma-method [12, 14, 17, 18] in constructing the recommended dependence. This circumstance allows us to state that the values of the volume thermal expansion coefficient of liquid iron obtained in present work are the most reliable and can be recommended as reference data.

Table 4. Comparison of the results of this work with literature data (in order of decreasing deviation of the VTEC from our data).

| Reference | Year | Method | Temperature interval (K) | Purity (wt. %) | \( \delta\rho_m(T_f) \) | \( \delta\beta_m(T_f) \) |
|-----------|------|--------|--------------------------|---------------|-----------------|-----------------|
| [4]       | 1960 | MBP    | 1849–2000               | 99.95         | -0.43           | 142.9           |
| [5]       | 1964 | MBP    | 1810–1895               | 99.98         | 0.06            | 101.6           |
| [6]       | 2006 | EML    | 1766–1855               | —             | -0.38           | 77.2            |
| [7]       | 2003 | P      | 1817–1878               | 99.99         | -0.36           | 59.5            |
| [8]       | 2006 | R      | 1809–2480               | —             | -0.45           | 52.0            |
| [9]       | 1963 | A      | 1800–2500               | 99.9          | -0.75           | 45.4            |
| [10]      | 2016 | EML    | 1753–1937               | 99.5          | -0.38           | 34.8            |
| [11]      | 1969 | SD     | 1811–2123               | 99.98         | -0.12           | 19.4            |
| [12]      | 1979 | GM     | 1543–2050               | 99.99         | -0.08           | 12.1            |
| [13]      | 2013 | EML    | 1558–1808               | —             | -1.1            | -8.3            |
| [14]      | 1974 | GM     | 1812–1993               | 99.98         | 0.16            | 6.1             |
| [15]      | 1994 | GM     | 1809–1953               | 99.98         | -1.25           | -5.3            |
| [16]      | 1972 | A      | 1773–1973               | 99.96         | -0.61           | 2.0             |
| [17]      | 1981 | GM     | 1830–2306               | 99.95         | -0.74           | 1.9             |
| [18]      | 1972 | GM     | 1810–1923               | —             | -0.25           | -0.1            |

Conclusions

New experimental data on the density and thermal expansion coefficients of pure iron in solid and liquid states are obtained. Relative density changes on allotropic trasformations and solid – melt phase
transition are directly measured. Good agreement between the obtained results and the most reliable literature data is shown.

Acknowledgments
The study was carried out under state contract with IT SB RAS (AAAA-A17-117022850029-9).

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