Heat transfer coefficients of praseodymium in condensed state

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Abstract. The thermal diffusivity and the thermal conductivity coefficients of praseodymium have been investigated by the laser flash technique with an error of 3–6% in the temperature range from 295 to 1625 K of the solid and liquid states, including the regions of phase transitions. Comparison of measurement results with the available literature data was carried out. The fitting equations and the table of reference data on the heat transfer coefficients of praseodymium for scientific and practical use have been developed.

1. Introduction
The active study of the properties of lanthanides has begun in the late 50s of the last century, when the methods of their separation and purification were developed and metals with a relatively low content of impurities were obtained. The raised interest to the study of their properties is caused both the prospects of widespread use of the rare-earth metals (REM) in apparatus and the possibility of solving the most important task consisting in determining the relationship of the electronic composition of a substance with its structure and macroscopic properties. However, many properties of the REM were not studied experimentally or were investigated in scarce.

The thermal diffusivity and thermal conductivity of praseodymium (Pr) in the condensed state at normal pressure were studied in quite a large number of works [1–10], however the available data do not agree well together. The thermal diffusivity anomalous change in the region of existence of α-phase was observed in [7, 8]. The high temperature β-phase and the liquid phase have been studied worst of all. The discrepancy between the results from different sources exceeds 40%. Thereby, the main objective of this study was to determine experimentally the thermal conductivity and thermal diffusivity of praseodymium in the temperature interval of 295–1625 K in the condensed state, including the regions of phase transformations.

2. Experimental technique
The laser flash method was used to measure the thermal conductivity (λ) and thermal diffusivity (α) of praseodymium. The main experiments were carried out on the LFA-427 installation [11]. The samples were cut from ingot of praseodymium of brand PrM-2 with a purity of 99.91 wt. %. The main impurities were Ca – 0.001%, Ce – 0.04%, Cr – 0.0014%, Cu – 0.0028%, Eu – 0.0003%, Fe – 0.007%, La – 0.0006%, Mo – 0.0002%, Nb – 0.00076%, Nd – 0.021, Ni – 0.0014%, Pd – 0.00073%, Sm – 0.009%, Ta – 0.0004%. The presence of impurities in the studied metal was determined by the methods of mass spectroscopy and atomic-emission spectroscopy.

At temperatures below 1000 K the experiments were carried out by the standard technique for the samples in “free” state, which has been described in detail in [12] and has already been tested by the
authors of this article for solid REMs [13, 14]. A cylindrical specimen with plane-parallel polished ends with a diameter of 12.6 mm and a thickness of 2.5 mm was used. The experiments were carried out in “dry” vacuum ~2×10⁻⁵ mbar in several heating-cooling cycles. The thermal diffusivity was calculated according to the computational model proposed by Cape and Lehman [15]. A correction for the laser pulse finite duration and its real shape was introduced according to [16].

High plasticity and chemical activity of Pr in the high temperature β-phase made it difficult to carry out measurements on “free” samples. Thus, experiments at above 1000 K were performed on specimens that were sealed into a tantalum cell, whose construction and characteristic geometric dimensions were similar to the cell described in [17]. The preparation, cleaning and annealing of the sample, as well as the method of sealing the tantalum cell with the investigated REM are described in detail in our articles, in which such approach is well tested in experiments with liquid neodymium [18] and samarium [19]. The computational model introduced in [17], as well as our data on the density [20] and heat capacity [21] of praseodymium were used to obtain the values of λ and a. The thermal diffusivity measurement errors of “free” and sealed samples that were estimated by the method [17] were 2–3% and 4–6%, respectively. The thermal conductivity error of the melt and β-phase almost coincides with the thermal diffusivity error, but it increases to 3–4% for the α-phase due to the error of the density [20] and heat capacity [21] data, which are used in recalculation of a to λ.

3. Results and discussion

The thermal diffusivity measurement results on Pr are shown in figure 1. One can see that the data obtained in experiments with “free” sample and cell in the heating-cooling cycles in the α-phase are reproduced among themselves. The temperature dependence of a in the α-phase at ~640 K has a local minimum characteristic of the second-order phase transition. Such behavior of a has also been established in our experiments with Nd [18] and Sm [19]. The reason for this phenomenon is not clear, since there are no structural and magnetic phase transitions in the temperature range of 295–1000 K.

Since a(T) of Pr is not monotonous and has features, then the entire investigated interval was divided into 4 areas, in each of which the results were approximated by following polynomials:
\[
\alpha(T) = 8.44 + 0.92 \times 10^{-2} T - 9.91 \times 10^{-6} T^2, \quad 295 \leq T \leq 636 \text{ K}, \quad (1)
\]
\[
\alpha(T) = 8.50 + 3.99 \times 10^{-3} T - 1.88 \times 10^{-6} T^2, \quad 636 \leq T \leq 1075 \text{ K}, \quad (2)
\]
\[
\beta(T) = -30.74 + 7.954 \times 10^{-2} T - 3.775 \times 10^{-5} T^2, \quad 1075 \leq T \leq 1220 \text{ K}, \quad (3)
\]
\[
\alpha(T) = 3.56 + 0.53 \times 10^{-2} T, \quad 1220 \leq T \leq 1625 \text{ K}, \quad (4)
\]

where \( T \) is the temperature in K, \( \alpha \) is in \( 10^{-6} \text{ m}^2 \text{ s}^{-1} \). The standard deviations of the experimental points from the approximation dependences (1)–(4) do not exceed 0.55, 0.5, 0.9 and 0.55%, respectively. The recommended \( \alpha \) values, calculated \( \lambda \) data, as well as available \( \rho \) and \( c_p \) data of praseodymium are presented in the Table.

**Table.** The recommended values of praseodymium thermophysical properties.

| \( T, \text{ K} \) | \( \alpha, 10^{-6} \text{ m}^2 \text{ s}^{-1} \) | \( \lambda, \text{ W} (\text{m K})^{-1} \) | \( \rho, \text{ kg m}^{-3} \) [20] | \( c_p, \text{ J} (\text{g K})^{-1} \) [21] |
|---|---|---|---|---|
| 300 | 10.31 | 13.67 | 6764 | 0.197 |
| 400 | 10.53 | 15.76 | 6755 | 0.220 |
| 500 | 10.56 | 17.20 | 6744 | 0.243 |
| 600 | 10.39 | 17.97 | 6730 | 0.257 |
| 700 | 10.37 | 18.80 | 6714 | 0.270 |
| 800 | 10.49 | 19.89 | 6695 | 0.283 |
| 900 | 10.57 | 20.90 | 6674 | 0.296 |
| 1000 | 10.61 | 21.83 | 6650 | 0.309 |
| 1075 | 10.62 | 22.47 | 6630 | 0.319 |
| 1075 | 11.14 | 22.19 | 6629 | 0.301 |
| 1100 | 11.08 | 22.03 | 6619 | 0.301 |
| 1200 | 10.35 | 20.46 | 6581 | 0.301 |
| 1220 | 10.11 | 19.97 | 6573 | 0.301 |
| 1220 | 10.03 | 25.26 | 6563 | 0.384 |
| 1300 | 10.45 | 26.16 | 6526 | 0.384 |
| 1400 | 10.98 | 27.27 | 6480 | 0.384 |
| 1500 | 11.51 | 28.39 | 6434 | 0.384 |
| 1600 | 12.04 | 29.51 | 6388 | 0.384 |
| 1625 | 12.17 | 29.79 | 6376 | 0.384 |

The comparison of our results on the thermal diffusivity with data from [1–10] is shown in figure 2. Since non-steady-state measurement methods were used in most studies, with the exception of [1–3], and the measured value was the thermal diffusivity, then that value was compared. Results of \( \alpha \), given in figure 2 for [1–3], were calculated from \( \lambda \) using the data on \( \rho \) [20] and \( c_p \) [21]. It can be seen that our recommended values in the region of the \( \alpha \)-phase existence are consistent with experimental data of [1–3, 9, 10] within the total measurement errors. Our results at temperatures of up to 610–660 K are consistent with the data of [6–8] within the total measurement errors; however, there are significant deviations from the results of these works above the specified temperatures. This is caused by the presence of extremes on the temperature dependences of \( \alpha \), which are similar to the change in \( \alpha \) during second-order phase transitions. Authors of [6–8] indicate that a possible cause of the \( \alpha(T) \) anomalous change is the rearrangement of the electronic subsystem and, in particular, the valence change. However, the monotonic dependence of the \( \alpha(T) \) in the region of existence of the \( \alpha \)-phase was obtained by the authors from the same group of scientists in later works [9, 10]. Unfortunately, the reasons for the anomaly appearance in [6–8] and its absence in [9, 10] were not discussed. Our experimental values agree with the results of [10] and [4] obtained for the \( \beta \)-phase and the liquid state, respectively.
within the total measurement errors and almost coincide with the single point obtained for the β-phase in [5]. Experimental results [5] are significantly higher (by about 30%) than our recommended values in the liquid phase and diverge among themselves within 12%.

Conclusion
New experimental data for the praseodymium heat transfer coefficients have been obtained in a wide range of temperatures of the solid and liquid states, including the phase transition regions. The comparison of obtained results with the available data was carried out. The fitting equations and the table of recommended values of studied transport properties have been developed for the use in various scientific and practical applications, as well as for inclusion in databases.

Acknowledgement
This work was carried out under the state contract with IT SB RAS (AAAA-A17-117022850029-9).

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