The thermal expansion of terbium over a wide temperature range

Yu M Kozlovskii, S V Stankus
Kutateladze Institute of Thermophysics SB RAS, 630090 Novosibirsk, Russia

E-mail: kozlovskii.yurii@gmail.com

Abstract. The results of a dilatometric study of the linear thermal expansion coefficient (LTEC) of polycrystalline terbium within the temperature range of 110–800 K are presented. The measurements were conducted with an error \((1.5\text{--}2.0)\times10^{-7}\text{K}^{-1}\). Approximate dependencies which allow calculating the reference tables of volumetric properties for the entire measurement interval were obtained. The character of the change in the linear thermal expansion coefficient in the vicinity of the Curie and Neel points is established. Critical exponents of the LTEC for two magnetic phase transitions were defined.

1. Introduction

Rare earth metals (REM) are widely used at the creation of materials with unique properties [1, 2]. Optimization of the processes of the synthesis of alloys and compounds of the REM requires knowledge of the thermophysical properties of the components ones of which are the pure elements of the lanthanide series. As well as the transition metals of the fourth period of the table of elements by D.I. Mendeleev, lanthanides are elements that exist in the ferromagnetic state and are the basis for creating magnets with record characteristics. For this reason the study of the properties of the REM gives important information for the development of theories of phase transitions.

Terbium, which refers to a subgroup of heavy REM, undergoes two magnetic transitions [3–5] in the low temperature range of 200–230 K. It is known that the results of dilatometric measurements [6, 7] make it possible to determine both the temperatures of phase transition and change of the linear thermal expansion coefficient (LTEC) over the region of the magnetic transition. Unfortunately, studies of the thermal expansion of terbium [8–10], performed in the 50-60s of the last century, don’t give detailed information about the properties change in the region of phase transition since the results are shown only in the form of small graphs. In addition, the discrepancies between the data of different authors for the LTEC significantly exceed the estimated measurement errors and reach 22%. The purpose of this paper is to study the thermal expansion of polycrystalline terbium, especially in the regions of magnetic phase transformations, and to determine the critical exponents at the Curie and Neel points.

2. Material, method, and experimental equipment

Distilled terbium, previously melted in a tantalum crucible, with a purity of 99.83 mass. % was used to prepare the samples. The main impurities: Fe — 0.01%; Ca — 0.01%; Cu — 0.03%; refractory metals — 0.02%; others REM — 0.1%. Polycrystalline samples 25 mm in length and 6 mm in diameter were annealed in vacuum during 4 hours at a temperature of 1173 K.
The thermal expansion of terbium was investigated using a DIL-402C horizontal dilatometer [11] with holder and pushrod made of fused silica or sintered alumina. The sample was mounted on a stand made of holder material and was clamped between the holder and pushrod with a load of 45 cN which was held constant during the experiment. The elongation was measured by an inductive linear variable displacement transducer (LVDT) with a resolution better than 1 nm. The temperature was measured by Type E (for low temperatures) and Type S (for high temperatures) thermocouples. The hot junction of the thermocouple was located in direct proximity to the lateral surface of the sample. The measurements were carried out within the temperature range of 110–800 K during heating and cooling at a rate of 0.5 or 2 K/min, and 20 min isothermal exposure at maximum and minimum temperatures. Before the experiment the setup was evacuated (up to 1 Pa) and filled with helium (99.995 vol. % pure) which was additionally purified by special device for cleaning and drying of inert gases — EPISHUR-A 11 SL [12]. A detailed description of the experimental technique was given in the previous paper [6].

The nonlinearity of the displacement transducer, differences in the temperatures and in the LTECs of the holder and pushrod materials, etc. are taken into account by the measurement of the correction function of the dilatometer. The correction function was determined on standard samples of fused silica (for low temperatures) and sintered alumina (for high temperatures) with 25 mm in length and 6 mm in diameter certified by NETZSCH. The conditions for these tests were identical to those of the main experiments. The correction function determined in this way was reproduced within 0.2 μm.

Measurement results are given as the temperature dependence of the relative elongation ε of the sample under heating or cooling:

\[
\varepsilon(T) = \left( L(T) - L_{293} \right) / L_{293},
\]

where \( L_{293} \) and \( L(T) \) are the sample length at 293.15 K and at \( T \), respectively. The LTEC \( \alpha \), and the true LTEC \( \alpha' \) are determined as follows:

\[
\alpha(T) = \frac{1}{L_{293}} \left( \frac{\partial L}{\partial T} \right)_p = \left( \frac{\partial \varepsilon}{\partial T} \right)_p,
\]

\[
\alpha'(T) = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p = \frac{\alpha(T)}{1 + \varepsilon(T)},
\]

where \( p \) is the pressure.

The temperature dependence of the LTEC was found by direct numerical differentiation of the raw experimental data on relative elongation:

\[
\alpha(T_i) = \frac{1}{2} \left( \varepsilon_{i+1} - \varepsilon_i + \varepsilon_i - \varepsilon_{i-1} \right) / \left( T_{i+1} - T_i \right),
\]

where \( \varepsilon = \varepsilon(T) \) is the relative elongation of the sample at the temperature \( T_i \). Such approach makes it possible to obtain directly the temperature dependence of the LTEC, without differentiating the approximation equation for the relative elongation. The last one introduces an additional error into the \( \alpha \) associated with the ambiguity in the choice of the fitting equation for \( \alpha(T) \), and also doesn’t reveal the behavior of the LTEC in the region of phase transformations.

The systematic error of the LTEC was determined in experiments with samples of high-purity aluminum, copper (99.99 mass % pure), and platinum (99.93 mass % pure) 25 mm in length under conditions identical to those of the main experiments with terbium. The results showed that the difference between the data obtained in the present work and the reference data of the LTEC [13, 14] doesn’t exceed (1.5–2) × 10^{-7} K^{-1} (or 3%) and on average is 8 × 10^{-8} K^{-1}. 

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3. Results and Discussion

The experiments were carried out in two stages: at low and high temperatures. The obtained data were «sewed together» in overlapping regions. The temperatures of the boundaries of the regions were determined from the condition of equality of the LTEC. As can be seen from figure 1 on the dependences $\alpha(T)$ of the terbium, two minimums are observed.

Anomalies are associated with magnetic phase transformations occurring in terbium: paramagnet-antiferromagnet at the Neel temperature ($T_N$) and antiferromagnet-ferromagnet at the Curie temperature ($T_C$). An analysis of the data obtained in various regimes has shown that more reliable data were obtained during heating for the Curie point and during cooling for the Neel point since of the proximity of the Curie and Neel points.

The minimum of the LTEC for the antiferromagnet-ferromagnet transition was observed at:

$$T_C = 219\pm1.5 \, \text{K};$$

$$\alpha(T_C) \times 10^{-6} \, \text{K}^{-1} = -19.8\pm1.0,$$

and the paramagnet-antiferromagnet at:

$$T_N = 227.7\pm1.5 \, \text{K};$$

$$\alpha(T_N) \times 10^{-6} \, \text{K}^{-1} = -21.45\pm1.0.$$

Outside the temperature intervals immediately adjacent to the Curie and Neel points the data were fitted with equations of the form:

$$\alpha(T) = \sum_{i=0}^{k} A_i t^i,$$

where $t = T - 273.15 \, \text{K}$.

In the regions of magnetic phase transitions the treatment was performed by using scaling dependences [15]. The magnetic contribution was obtained from the values of $\alpha^*(T)$:
\[ \alpha_{\text{mag}}^*(T) = \alpha^*(T) - \alpha_{\text{para}}^*(T), \]

where \( \alpha_{\text{para}}^*(T) \) is an approximation of the experimental data within the temperature interval of 400–700 K of the paramagnetic terbium state:

\[ \alpha_{\text{para}}^*(T) = 4.56205 - 6.74652 \times 10^{-3} T, \]

where \( T \) is in K, \( \alpha \) is in \( 10^{-6} \) K\(^{-1}\).

The magnetic component of the true LTEC was written in the form:

\[ \alpha_{\text{mag}}^* = A|\tau|^a + B, \]

where \( A, B \) are constants, \( a \) is the critical exponent of the true LTEC, and \( \tau = \left( T - T_{C(N)} \right) / T_{C(N)} \). It is obvious, that \( B = \alpha_{\text{mag}}^*(T_{C(N)}) \). Then, using \( Y_{\text{mag}} = \alpha_{\text{mag}}^* - \alpha_{\text{mag}}^*(T_{C(N)}) \) and equation (6):

\[ \ln(Y_{\text{mag}}) = \ln(A) + a \ln(|\tau|). \]

As is seen from (7), it is possible to calculate the values of the critical amplitude \( A \) and the critical exponent \( a \) by performing the linear approximation of \( \ln(Y_{\text{mag}}) \). The obtained values of the critical exponents calculated for different regimes are given in tables 1, 2. Coefficients of the equation (4) are presented in table 3.

**Table 1.** Critical exponents of LTEC for terbium in the region of the Curie point.

| Regime | Below Curie point | Above Curie point |
|--------|------------------|------------------|
|        | \( \alpha \)     | \( \alpha \)     |
| Heating| 0.88±0.22        | 1.29±0.64        |
| Heating| 1.23±0.14        | 2.31±0.76        |
| Heating| 0.95±0.10        | 2.17±0.20        |
| Cooling| 1.01±0.13        | 2.03±0.48        |
| Average| 1.02±0.15        | 1.95±0.52        |

**Table 2.** Critical exponents of LTEC for terbium in the region of the Neel point.

| Regime | Below Neel point | Above Neel point |
|--------|------------------|------------------|
|        | \( \alpha \)     | \( \alpha \)     |
| Cooling| 1.81±1.02        | 2.07±0.37        |
| Cooling| 2.09±0.19        | 1.86±0.30        |
| Cooling| 2.21±0.14        | 1.89±0.12        |
| Average| 2.04±0.45        | 1.94±0.26        |

Figure 2 shows a comparison of the results obtained for the LTEC with [9]. It can be seen that the results agree well in the low temperature region, and our data describe the regions of the Curie and Neel points in much greater detail. At high temperatures the data of [9] are somewhat higher than those obtained in this work. Perhaps this is a consequence of the different purity of the studied samples and the features of their preparation. The measurement error in [9] is not indicated. The maximum difference at temperatures above room doesn’t exceed 15%, while at low temperatures doesn’t exceed 7%.
Table 3. Coefficients of the equation (4).

| Region | T, K   | $A_0$, K$^{-1}$ | $A_1$, K$^{-1}$ | $A_2$, K$^{-1}$ | $A_3$, K$^{-1}$ | $A_4$, K$^{-1}$ |
|--------|--------|----------------|----------------|----------------|----------------|----------------|
| 1      | 110–213| −195.138       | 5.2967         | −51.3169×10$^{-3}$ | 21.9151×10$^{-5}$ | −35.5987×10$^{-8}$ |
| 2      | 213–219| 334.506        | −1.6178        | —              | —              | —              |
| 3      | 219–220| −1189.26       | 5.34           | —              | —              | —              |
| 4      | 220–227| −6296.34       | 56.6766        | −12.783×10$^{-2}$ | —              | —              |
| 5      | 227–227.7| 1197.07       | −5.3514        | —              | —              | —              |
| 6      | 227.7–230| −2129.556   | 925.826×10$^{-2}$ | —              | —              | —              |
| 7      | 230–248| −2505.81       | 28.6521        | −10.9069×10$^{-2}$ | 13.8524×10$^{-5}$ | —              |
| 8      | 248–287| −197.371       | 202.634×10$^{-2}$ | −6.7642×10$^{-3}$ | 7.574×10$^{-6}$ | —              |
| 9      | 287–522| −20.196        | 21.91×10$^{-2}$ | −6.7454×10$^{-4}$ | 9.4205×10$^{-7}$ | −4.8881×10$^{-10}$ |
| 10     | 522–800| 7.479          | −3.587×10$^{-3}$ | 9.049×10$^{-6}$ | —              | —              |

Figure 2. Recommended data for the thermal expansion of terbium

1 — [9] heating; 2 — [9] cooling; 3 — this work.

4. Conclusion

Experimental data on the linear thermal expansion coefficient of polycrystalline terbium were obtained with high accuracy for the first time. The regions of magnetic phase transformations are studied in detail and critical exponents of LTEC at the Curie and Neel points are defined. All critical exponents are positive and substantially exceed the critical exponent −0.12 for the specific heat in absolute value. The paper presents recommended approximation equations applicable over a wide temperature range. This allows creating detailed data tables of the thermal expansion and the relative elongation.

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