Structural Study, Mössbauer Spectra and Electrical Properties of R₅Fe₆Sn₁₈ (R = Tm, Lu) Compounds

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Ternary intermetallic R₅Fe₆Sn₁₈ (R = rare earth element, M = Co, Ru, Rh, Os, Ir) compounds have been synthesized from the elements by arc melting, annealed at 670 K and characterized by X-ray powder diffraction and energy dispersive X-ray analyses. Performed structure refinements have shown that they crystallize in the cubic TbRh₆Sn₁₈ structure type (space group Fm-3m, a = 13.55399(4) Å, a = 13.53243(5) Å for Tm and Lu compounds, respectively). Using ⁵⁷Fe Mössbauer spectroscopy it has been found that the magnetic state of the Fe atoms in the Tm₅Fe₆Sn₁₈ and Lu₅Fe₆Sn₁₈ stannides is paramagnetic. The value of the isomer shifts for Lu₅Fe₆Sn₁₈ and Tm₅Fe₆Sn₁₈ is positive relative to pure Fe. The ⁵⁷Fe Mössbauer spectra for Lu₅Fe₆Sn₁₈ and Tm₅Fe₆Sn₁₈ stannides have shown that the quadrupole splitting for the Fe position (24e) has magnitudes of 0.43 and 0.45 mm/s, respectively. The similarity of these values is consistent with a qualitative crystal structure analysis. The examined Tm₅Fe₆Sn₁₈ and Lu₅Fe₆Sn₁₈ compounds have been characterized by metallic-like conductivity and high values of electrical resistivity (672.9 μΩ cm, 623.8 μΩ cm at 300 K for Tm and Lu, respectively).

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1. Introduction

The series of RM₅Sn₂₆ intermetallics (R = rare earth element, M = Co, Ru, Rh, Os, Ir) is characterized by several types of the crystal structures indicated as phases I, II, III, V, and VII [1–3]. The RM₅Sn₂₆ compounds were analyzed in detail and discussed by Skolozdra in Ref. [4]. These compounds are interesting because some of them show superconductivity and magnetic ordering. The main feature of these phases is a mixture of rare earth and tin atoms in one of the crystallographic positions, and the presence of the metallic and covalent bonding. The phase I of stannides with the formula R₅M₆Sn₁₂ has a simple cubic structure (space group Pm-3m) with the lattice parameter a = 0.97 nm. In Ref. [5] the authors described the structure of the phase I (Yb₂Rh₄Sn₁₃-type) as a three-dimensional array of corner-sharing trigonal prisms with Rh atoms in the centers. The phase III according to X-ray data has a cubic structure (space group F-43m, a = 1.37 nm) with the formula Tb₅Rh₄Sn₁₈ [6]. For stannides with the formula Sn₄M₆Sn₁₈ two structure types were found corresponding to phases II and II’. The structure of the phase II is tetragonal (space group I₄₁/acd) while the phase II’ has a cubic structure with the space group Fm-3m. X-ray and electron diffraction investigations of the TbRh₄Sn₁₈ and DyOs₄Sn₁₈ single crystals showed that they can be considered as a disordered microtwinned phase II and these compounds were named as II’ phases (space group Fm-3m) [7]. The structure disordering of the Tb₅Rh₆Sn₁₈ stannide concerned the Tb(2) and Sn(2) sublattices of the formula [Sn(1)₁₋ₓTbₓ][Tb(2)₁₋ₓRhₓSn(2)₁₋ₓSn(3)₁₋ₓSn(4)₁₋ₓ] [7]. In the Tb₄(Tb₀₆Sn₄₀)[Rh₆Sn₁₈-type a statistical occupation of the 4a sites by terbium and tin atoms was observed [7]. The magnetic and electrical properties of the RM₅Sn₂₆ stannides were studied for determination of the superconducting behavior [1–3, 8, 9]. The relation between the crystal structure and superconducting properties of the [Sn₁₋ₓErₓ]Er₄Rh₆Sn₁₈ phase was analyzed in Ref. [9], where the influence of the variation in (Sn, Er) occupation of the [Sn₁₋ₓErₓ]Er₄ sublattice upon low temperature properties was observed. The investigation of the R–Ni–Sn ternary systems in the region of high tin concentrations resulted in the discovery of R₅–ₓSnₓNi₁₂Sn₂₄ₓ₊₁ cubic phases with a GdNi₂Sn₅ type structure [10]. The similar occupation of the crystallographic 2a position by a mixture of R and Sn atoms was observed for these phases, and a crystal structure analysis showed slightly different compositions for the representatives of this structure type varied from R₄Ni₁₂Sn₂₅ (for Dy) to R₅Ni₁₂Sn₄₈ (for La) [10, 11].

In this paper the synthesis and the results of crystal structure, ⁵⁷Fe Mössbauer spectroscopy, and electrical properties studies of the new Tm₅Fe₆Sn₁₈ and Lu₅Fe₆Sn₁₈ compounds are reported.
2. Experimental details

Samples with the nominal composition $R_{12}Fe_{20}Sn_{65}$ ($R = \text{Tm,} \text{ and Lu}$) were prepared using an electric arc furnace by direct arc melting of the constituent elements (overall purity: $R = 99.9$ wt%, $\text{Fe} = 99.99$ wt%, $\text{Sn} = 99.999$ wt%) in a protective argon atmosphere. The alloys were subsequently annealed at 670 K for 720 h and then cold water quenched. The compositions of the obtained samples were examined by scanning electron microscopy (SEM) using the scanning electron microscope REMMA-102-02. A quantitative electron probe microanalysis (EPMA) of the phases was carried out using an energy-dispersive X-ray analyzer with pure elements as standards (acceleration voltage was 20 kV; $K$- and $L$-lines were used).

X-ray powder diffraction (XRPD) data were collected in the transmission mode on a STOE STADI P diffractometer (linear PSD detector, $2\theta/\omega$-scan; Cu $K_{\alpha}$ radiation, curved germanium (1 1 1) monochromator). The crystal structures were refined by the Rietveld method [12] with the FullProf.2k program (version 4.80) [13] from the WinPLOTR program package [14] applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters.

The Mössbauer spectra were recorded in the transmission mode. A WISSEL Mössbauer spectrometer and a source of $^{57}$Co gamma-quanta in a Cr matrix were used for measurements. The equipment was characterized by the line-width of 0.22 mm/s for the gamma-quanta source. The calibration of isomeric shift values was carried out relative to $\alpha$-Fe at room temperature.

The electrical resistivity was measured on millimeter-scale, with well-shaped pieces cut by spark erosion from the polycrystalline samples by the standard two-probe technique in the temperature range 10.5–300 K using a helium cooler with a reserved cycle (Advanced Research Systems, USA). The temperature dependence of the magnetic susceptibility was measured by the Faraday method in the 78–300 K temperature range and under a magnetic field up to 0.8 T.

3. Results and discussion

The analysis of the positions of diffraction peaks and their intensities of the $\text{Tm}_{12}\text{Fe}_{20}\text{Sn}_{65}$ and $\text{Lu}_{12}\text{Fe}_{20}\text{Sn}_{65}$ compounds led to a cubic structure of the $\text{Tb}_{6}(\text{Tb}_{0.6}\text{Sn}_{0.4})\text{Rh}_{6}\text{Sn}_{18}$-type [7] (the so-called phase II, space group $Fm\text{-}3m$). The experimental conditions of the structure refinements and crystallographic

| Experimental details and crystallographic data for $R_{12}Fe_{20}Sn_{65}$ ($R = \text{Tm, Lu}$) compounds | $\text{Tm}_{12}\text{Fe}_{20}\text{Sn}_{65}$ | $\text{Lu}_{12}\text{Fe}_{20}\text{Sn}_{65}$ |
|-----------------------------------------------|---------------------------------|---------------------------------|
| **Formula** | $\text{Fe}_{20}\text{Sn}_{18}$ | $\text{Fe}_{20}\text{Sn}_{18}$ |
| space group – Wyckoff sequence / Pearson symbol | $Fm\text{-}3m \ (\text{No. 225})$ | $kF^2_{\text{c}c}/ cF196 \ - \ 80$ |
| structure type | $\text{Tb}_6(\text{Tb}_{0.6}\text{Sn}_{0.4})\text{Rh}_6\text{Sn}_{18}$ | $\text{Sn}_{18}$ |
| $Mr / Z$ | 3316.52 / 4 | 3346.68 / 4 |
| lattice parameter $a$ [Å] | 13.55399(4) | 13.53243(5) |
| cell volume $V$ [Å$^3$] | 2490.013(11) | 2478.151(15) |
| calculated density $D_r$ [g/cm$^3$] | 8.846 | 8.909 |
| absorption coefficient $\mu$ (Cu $K_{\alpha}$) [mm$^{-1}$] | 199.10 | 204.65 |
| specimen shape / particle morphology / colour | Flat sheet (8 x 8 x 0.1 mm) / loose powder, grain size < 0.04 mm / light-grey |
| data collection temperature $T$ [K] | 297(1) |
| diffractometer | STOE STADI P (Transmission mode) |
| radiation, wavelength $\lambda$ [Å] | Cu $K_{\alpha}$, 1.540598 |
| angular range for data collection / increment $2\theta$ [°] | 6.000 ≤ $2\theta$ ≤ 110.045 / 0.015 | 6.000 ≤ $2\theta$ ≤ 110.045 / 0.015 |
| linear PSD step $2\theta$ [°] / time [s/step] | 0.480 / 375 | 0.480 / 375 |
| number of measured reflections | 115 | 115 |
| number of refined parameters | 19 | 19 |
| reliability factors: | | |
| $R_I = \Sigma|I_{\text{obs}} - I_{\text{calc}}| / \Sigma|I_{\text{obs}}|$ | 0.0245 | 0.0154 |
| $R_F = \Sigma|F_{\text{obs}} - F_{\text{calc}}| / \Sigma|F_{\text{obs}}|$ | 0.0264 | 0.0209 |
| $R_R = \Sigma|y_{\text{c}} - y_{\text{c},\text{calc}}| / \Sigma|y_{\text{c}}|$ | 0.0303 | 0.0340 |
| $R_{\exp} = \Sigma[w_{\text{c}}|y_{\text{c}} - y_{\text{c},\text{calc}}|^2 / \Sigma w_{\text{c}}y_{\text{c}}^2]^{1/2}$ | 0.0385 | 0.0443 |
| $R_{\exp} = \{[n-p(\Sigma w_{\text{c}}y_{\text{c}}^2)]^{1/2}$ | 0.0371 | 0.0440 |
| $\chi^2 = (R_{\exp}/R_{\exp})^2$ | 1.08 | 1.02 |
| content of $R_{5}Fe_{6}Sn_{18}$ / FeSn$_2$ / Sn phases [wt%] | 91.5(4) / 6.7(1) / 1.8(1) | 93.2(4) / 4.1(1) / 2.7(1) |
data for the Tm$_2$Fe$_6$Sn$_{65}$ and Lu$_2$Fe$_6$Sn$_{65}$ samples are summarized in Table I. Other types of the related structures, i.e., the so-called phase II (tetragonal Er$_4$(Er$_{0.33}$Sn$_{0.67}$)Rh$_6$Sn$_{18}$-type, space group $I4_1/acd$ [15]) and phase III (cubic Tb$_3$Rh$_6$Sn$_{17}$-type, space group $F-43m$ [5]) according to the classification of Ref. [1], were tested and rejected. The final atomic and isotropic displacement parameters for both compounds are given in Table II.

**TABLE II**

Fractional atomic coordinates, equivalent isotropic displacement parameters $B_{iso}$ [Å$^2$] and site occupancies $G$

| Site | R | Wyckoff position | $x$  | $y$  | $z$  | $B_{iso}$ [Å$^2$] | $G$  |
|------|---|------------------|------|------|------|-------------------|-----|
| Fe   | Tm | 24c              | 0.2554(3) | 0 | 0 | 0.43(6) | 1 |
|       | Lu | 25c              | 0.2500(4) | 0 | 0 | 0.34(7) | 1 |
| R1   | Tm | 4a               | 0 | 0 | 0 | 1.22(7) | 1 |
|       | Lu | 4a               | 0.3672(7) | 0.3672(7) | 0.3672(7) | 1.07(5) | 0.5 |
| R2   | Tm | 32f              | 0.3668(5) | 0.3668(5) | 0.3668(5) | 0.60(5) | 0.5 |
|       | Lu | 32f              | 0.4097(1) | 0.4097(1) | 0.4097(1) | 1.11(9) | 0.5 |
| Sn1  | Tm | 96k              | 0.1722(9) | 0.1722(9) | 0.1722(9) | 0.083(4) | 0.5 |
|       | Lu | 96k              | 0.1729(2) | 0.1729(2) | 0.1729(2) | 0.083(5) | 0.5 |
| Sn3  | Tm | 8c               | 1/4 | 1/4 | 1/4 | 1.71(3) | 1 |
|       | Lu | 8c               | 1/4 | 1/4 | 1/4 | 1.77(4) | 1 |

Recently we have published a report on the crystal structure of the Er$_2$Fe$_6$Sn$_{18}$ compound with Tb$_4$(Tb$_{0.6}$Sn$_{0.4}$)Rh$_6$Sn$_{18}$-type [16]. The full occupation of the 4n position was established exclusively by Er atoms in contrast to the parent Tb$_4$(Tb$_{0.6}$Sn$_{0.4}$)Rh$_6$Sn$_{18}$-type [7], where a statistical occupation of the 4a site by terbium and tin atoms was observed. A similar phenomenon is observed in the Tm$_2$Fe$_6$Sn$_{18}$ and Lu$_2$Fe$_6$Sn$_{18}$ compounds at 670 K: the Tm and Lu atoms fully occupied the 4a site corresponding to formula R$_2$Fe$_6$Sn$_{18}$. The obtained compositions of the both phases are in good agreement with the EPMA data (Tm$_{1.76}$Fe$_{19.65}$Sn$_{62.61}$ and Lu$_{1.76}$Fe$_{19.65}$Sn$_{62.81}$). Also, attention is drawn to the similarity of the values of atomic displacement parameters in the investigated structures and in the Tb$_4$(Tb$_{0.6}$Sn$_{0.4}$)Rh$_6$Sn$_{18}$ structure, i.e. small values are observed for Fe(Rh) atoms and the largest values are observed for Sn atoms in a tetrahedral coordination Sn[R$_4$] (8c site). The model of the Lu$_2$Fe$_6$Sn$_{18}$ structure and the stacking of coordination polyhedra are shown in Fig. 1.

The analysis of the interatomic distances (Table III) showed that the distances between Fe–Sn2, Fe–Sn1, Sn1–Sn1, and R2–Sn3 atoms are shorter than the sum of the respective atomic radii, which is probably caused by partial occupation of the crystallographic positions for R2, Sn1, and Sn2 atoms and a contribution of the covalence into the bond. The based Tb$_2$Rh$_6$Sn$_{18}$ structure is characterized by analogous shortening of interatomic distances between Rh–Sn and Tb–Sn atoms.

**Fig. 1.** Model of the Lu$_2$Fe$_6$Sn$_{18}$ structure (a) and stacking of cuboctahedrons in Lu$_2$Fe$_6$Sn$_{18}$ structure (b).

**Fig. 2.** Mössbauer spectrum of the Lu$_2$Fe$_6$Sn$_{18}$ stannide at room temperature.

**Fig. 3.** Mössbauer spectrum of the Tm$_2$Fe$_6$Sn$_{18}$ stannide at room temperature.

**Main interatomic distances in the R$_2$Fe$_6$Sn$_{18}$ (R = Tm, Lu) compounds [nm]**

| Atom       | Tm  | Lu  |
|------------|-----|-----|
| Fe–Sn2     | 0.2595 | 0.2593 |
| Fe–Sn1     | 0.2715 | 0.2715 |
| Fe–R2      | 0.2962 | 0.2964 |
| R1–Sn2     | 0.3304 | 0.3311 |
| R2–Sn3     | 0.2753 | 0.2739 |
| R2–Sn1     | 0.3130 | 0.3133 |
| R2–Sn2     | 0.3180 | 0.3167 |
| Sn1–Sn1    | 0.2448 | 0.2444 |
To study the magnetic state of iron atoms in the \( \text{Tm}_6\text{Fe}_5\text{Sn}_{18} \) and \( \text{Lu}_5\text{Fe}_6\text{Sn}_{18} \) compounds we used \(^{57}\text{Fe} \) Mössbauer spectroscopy. The corresponding Mössbauer spectra obtained for the \( \text{Lu}_5\text{Fe}_6\text{Sn}_{18} \) and \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \) compounds are shown in Figs. 2, 3, and their parameters are presented in Table IV.

Table IV

| Compound      | \( A \) [%] | IS [mm/s] | QS [mm/s] | \( G \) [mm/s] |
|---------------|-------------|-----------|-----------|----------------|
| \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) | 100         | 0.41 ± 0.02 | 0.33 ± 0.02 | 0.26           |
| \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \) | 100         | 0.44 ± 0.02 | 0.36 ± 0.02 | 0.27           |

In the absence of an external magnetic field there is no magnetic splitting in the spectrum of \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) and \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \), indicating either the absence of a magnetic moment at the Fe site or spin relaxation, and then \( L \gg \mu_0 \). To clarify the situation, the sample should be exposed to an external magnetic field \( H_{\text{ext}} \).

Here \( A \) (%) is the contribution of the respective subprofile to the total absorption profile, and the Mössbauer spectroscopy parameters are: the isomer (total) shift versus \( \alpha\)-Fe IS [mm/s], quadrupole splitting [QS (mm/s)], absorber line-width \( G \) [mm/s].

The value of the isomer shift (IS) for \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) and \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \) compounds is positive and slightly higher than unmeasured chemical shifts in the studied RFeSn6 stannides (\( R = \text{Tm}, \text{Yb}, \text{Lu} \)) [17, 18] or other intermetallic compounds containing iron [19, 20], for example in the Sc–Fe–Si systems, in which no magnetic moment was observed at Fe sites in the ternary compounds [19]. Those compounds have a small positive isomer shift relative to pure Fe. The shift sign indicates that the electronic density at Fe nuclei in those ternary compounds is less than that at the radiating Fe nuclei. It is well known that an increase in the number of \( d \)-electrons leads to a decrease in the density of \( s \)-electrons at the nucleus and indirectly results in a positive isomer shift. Of course, the importance of the contribution of the density of \( p \)-electrons to the value of the isomer shift should be noted, since similar to \( 3d \)-electrons, \( 4p \)-electrons shield \( s \)-electrons from the nucleus and indirectly determine the positive isomer shift. However, the screening effect of \( 4p \)-electrons is approximately 1.5 times weaker than the \( 3d \)-electron shielding effect. The absence of a local magnetic moment at the Fe atoms is confirmed by the absence of a magnetically split component in the Mössbauer spectrum. The values of the isomer shift and quadrupole splitting parameters indicate the paramagnetic nature of the magnetic interaction.

An extremely important parameter of the Mössbauer spectrum is the quadrupole splitting (QS). It characterizes the interaction of the electric quadrupole moments of the nuclei with internal crystal electric fields. The quadrupole moment of the nucleus \( \theta \) reflects the degree of deviation of its shape from the spherical one. As can be seen from the crystal structure cell (Fig. 1), the coordination number of the Fe atom is 12, and the coordination polyhedron is a slightly deformed cuboctahedron which is formed by 4Sn1 atoms (2.715 Å) and 8Sn2 atoms (2.593 Å). The \(^{57}\text{Fe} \) Mössbauer spectra for \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) and \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \) show that the quadrupole splitting for the Fe position (24e) have magnitudes of 0.43 and 0.45 mm/s, respectively. The similarity of these values is consistent with the above qualitative crystal structure analysis, which revealed that the Fe nearest neighbors are exclusively tin atoms (Fig. 1b), and the electric field gradient is determined for the most part by the tin atoms that are located at the vertices of the cuboctahedron and have reduced Fe–Sn distances.

Because of a strong covalent interaction between Fe and Sn atoms that surround them the increase in the population of \( d \)-states is due to the valence Sn electrons, and the number of Fe \( s \)-electrons is almost unchanged.

The measurements of the magnetic susceptibility of the \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) compound confirmed its paramagnetic state. Studied compound is characterized by small values of the magnetic susceptibility with values \( \chi = 25.42 \times 10^{-6} \) cm³/g at 78 K and \( \chi = 21.91 \times 10^{-6} \) cm³/g at 300 K. The analysis of the temperature dependence of the inverse magnetic susceptibility indicated that \( \chi^{-1}(T) \) behavior does not correspond to a modified Curie–Weiss law.

The examined \( \text{Tm}_5\text{Fe}_8\text{Sn}_{18} \) and \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) compounds are characterized by metallic-like conductivity in the temperature range from 10.5 K to 300 K and a large deviation from linearity of the temperature dependence of resistivity at high temperatures (Fig. 4). At low temperatures under cooling the resistivity predictably tends to a constant value (residual resistivity). As evident from Fig. 4, change of the resistivity caused by magnetic ordering was not observed on the \( \rho(T) \) dependence for the \( \text{Tm}_6\text{Fe}_8\text{Sn}_{18} \) compound up to 11 K. The temperature dependence parameters are presented in Table V. The absolute values of the resistivity of the \( \text{Tm}_6\text{Fe}_8\text{Sn}_{18} \) and \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) stannides are much higher (672.9 \( \mu \)Ω cm, 623.8 \( \mu \)Ω cm at 300 K for \( \text{Tm} \) and \( \text{Lu} \), respectively) than for the most intermetallics (Table V). As reported in the literature [1–4] most of the RM₆Sn₈ phases have a high resistivity values and authors concluded that one of the causes of high resistivity values is the presence of a significant ion-covalent contribution to the bonding.

Table V

| Compound | \( \rho_{290K} \) \( \mu \)Ω cm | \( \rho_{100K} \) \( \mu \)Ω cm | \( \rho_{290K} / \rho_{100K} \) | \( \rho_{290K} \) | \( \rho_{150K} \) | \( \rho_{290K} - \rho_{150K} \) \% |
|----------|-------------------------------|-------------------------------|-----------------------------|-----------------|-------------------|-----------------------------|
| \( \text{Tm}_6\text{Fe}_8\text{Sn}_{18} \) | 672.9 | 154 | 4.3 | 19.1 |
| \( \text{Lu}_5\text{Fe}_8\text{Sn}_{18} \) | 620 | 482 | 1.3 | 4.2 |

\( \rho_{\text{exp}} \) is the experimental resistivity value at 150 K and \( \rho_{\text{linear}} \) is the resistivity value at 150 K in the case of imaginary linear temperature dependence.
The observed character of the temperature dependence of electrical resistivity was discovered for the first time in actinides and was classified as anomalous [21, 22]. Then such the character of the temperature dependence of electrical resistivity was observed in many intermetallic compounds, such as YCo$_2$, Y$_4$Co$_3$, Y$_6$(Fe,Mn)$_{23}$, Er$_6$(Fe,Mn)$_{23}$ [23] and also for related series of the R$_5$$_x$Ni$_{12}$Sn$_{24+x}$ cubic phases with GdNi$_2$$_6$$_7$Sn$_5$.44 type structure [10]. One of the conditions for this type of the temperature dependence is the presence of a transition element in the compound, particularly a 3$d$-element.

Resistivity of a real sample can be written (taking into account the Matthissen rule) as

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{mag}(T),$$

where $\rho_0$ is the residual resistance, $\rho_{ph}(T)$ is the resistivity caused by the electron–phonon interaction, and $\rho_{mag}(T)$ is an additional component that contains various contributions from different physical mechanisms, such as Mott-type interband scattering, magnetic scattering (including scattering caused by the spin disordering in the presence of disordered magnetic moments) and other possible scattering mechanisms.

As noted above, the temperature dependences of the electrical resistivity of both Tm$_5$Fe$_6$Sn$_{18}$ and Lu$_5$Fe$_6$Sn$_{18}$ deviate from linearity. At high temperatures the observed decrease of the growth rate of resistivity cannot be correctly approximated by the Bloch–Grüneisen–Mott formula [24] within the studied temperature range. The Bloch–Grüneisen–Mott formula, which takes into account the Mott-type type interband scattering, describes experimental curves well in the case of slight nonlinearity. The greater deviation from the linearity narrows the temperature range within which the approximation is applicable. An approximation in a limited range loses the physical meaning to some extent if the approximation is based on an expression with the physical meaning behind it, as in the case of the Bloch–Grüneisen–Mott formula. Nevertheless (taking into account above remarks), we present the mentioned approximation for Lu$_5$Fe$_6$Sn$_{18}$ in Fig. 5 and provide some of its parameters.

Since the approximation by the Bloch–Grüneisen–Mott formula is impossible within the whole temperature range we can conclude that in our case the contribution of the transition metal to the total resistivity is not limited to the contribution to the residual resistivity, phonon component of scattering and Mott’s contribution, and $C_{mag}(T)$ has more constituents and determines complex nature of the temperature dependence of the resistivity of Lu$_5$Fe$_6$Sn$_{18}$.

In general, the character of the temperature dependences of the electrical resistivity of intermetallic compounds of such type depends on the constituents of a compound (whether it contains a magnetic or nonmagnetic rare-earth element, a magnetic or nonmagnetic transition element), magnetic ordering, and crystal structure. The $d$- and $f$-shells are influenced strongly by the interaction of surrounding ions, which can radically change the magnetic state of the ions.

In addition, the mentioned factors determine a relatively large absolute value of the resistivity of the Lu$_5$Fe$_6$Sn$_{18}$ compound. As for the tendency of the
growth rate of resistivity to decrease in the region of “high” temperatures with a temperature increase, one can recall the rule of Mooij [25], who suggested that if the average free path of conduction electrons decreases to the value of interatomic distances, then the resistivity shows a tendency to become temperature-independent.

4. Conclusion

In our work, crystal structure study of the new Tm$_5$Fe$_6$Sn$_{11}$5 and Lu$_5$Fe$_6$Sn$_{11}$8 stannides showed that both compounds crystallize in the cubic Tb$_5$Rh$_6$Sn$_{11}$8 structure type (space group $Fm-3m$) and enlarge the series of RM$_5$Sn$_y$ intermetallics. The full occupancy of the 4$a$ position by Tm and Lu atoms was established which corresponds to formula R$_5$Fe$_6$Sn$_{11}$8. Comparison of the shortening of interatomic distances between Fe–Sn and R–Sn atoms with Tb$_5$Fe$_6$Sn$_{11}$8 parent type was made.

The magnetic state of the Fe ion in Lu$_5$Fe$_6$Sn$_{11}$8 and Tm$_5$Fe$_6$Sn$_{11}$8 has been examined by $^{57}$Fe Mössbauer spectroscopy and it has been found to be paramagnetic. The values of the isomer shift for Lu$_5$Fe$_6$Sn$_{11}$8 and Tm$_5$Fe$_6$Sn$_{11}$8 have been found to be positive. The shift sign indicates that the electronic density at Fe nuclei in these compounds is less than that at the radiating nuclei of pure Fe. The $^{57}$Fe Mössbauer spectra for Lu$_5$Fe$_6$Sn$_{11}$8 and Tm$_5$Fe$_6$Sn$_{11}$8 showed that the quadrupole splitting for the Fe position (24$c$) have a value of 0.43–0.45 mm/s. The similarity of these values is consistent with a qualitative crystal structure analysis, which revealed that the Fe nearest neighbors are exclusively tin atoms, and the electric field gradient is determined for the most part by the tin atoms that are located at the vertices of the Fe coordination cuboctahedron and have reduced Fe–Sn distances. From both diffraction and Mössbauer data, the crystallographic data indicates the presence only one Fe site (24$c$) in the structure of the Tm$_5$Fe$_6$Sn$_{11}$8 and Lu$_5$Fe$_6$Sn$_{11}$8 compounds. In the electrical property measurements showed that the Tm$_5$Fe$_6$Sn$_{11}$8 and Lu$_5$Fe$_6$Sn$_{11}$8 compounds are characterized by metallic-like type of conductivity with high resistivity values similarly to the most related RM$_5$Sn$_y$ phases.

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