Neutron-Diffraction Study in TlFeS$_2$ and TlFeSe$_2$

at Low Temperatures

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Abstract—The crystal and magnetic structures of TlFeS$_2$ and TlFeSe$_2$ are studied by neutron diffraction in the temperature range of 10–320 K. The structures of TlFeS$_2$ and TlFeSe$_2$ have monoclinic symmetry with the space group $C2/m$ at room temperature. TlFeS$_2$ displays an antiferromagnetic phase at temperature below 200 K. The antiferromagnetic phase transition in TlFeSe$_2$ takes place at a temperature below 290 K. The temperature dependence of the unit-cell parameters and volume are obtained. The coefficients of thermal and linear expansion are calculated. The temperature dependences of the interatomic distances are presented.

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INTRODUCTION

The design of new generations of information systems and instruments for them, the development of microelectronics, the development of new nontraditional ecologically pure sources of energy constantly require the goal-directed search for and development of new materials with a set of specific physicochemical properties [1].

Layered and chain semiconductors with inherent strong anisotropy of the physical properties along different crystallographic directions occupy a special place amongst semiconductor crystals. One of the representatives of such crystal compounds with unique characteristics are the triple compounds TlFeS$_2$ and TlFeSe$_2$, which belong to the general group of compounds of the type TlMeX$_2$ (where Me is a 3$d$ metal, X = S, Se, Te) [2–4]. These semiconductors are quasi-one-dimensional antiferromagnets, ferro- or ferrimagnets. The triple compounds TlFeS$_2$ and TlFeSe$_2$ belong to the class of semiconductors with antiferromagnetic properties [2, 5].

At room temperature the crystal structures of TlFeS$_2$ and TlFeSe$_2$ have monoclinic symmetry with the space group $C2/m$ [6]. There are chain constructions of FeS$_4$ (or FeSe$_4$) tetrahedra with the common edges in the structures. Iron ions are at the center of the tetrahedra, and sulfur (or selenium) ions are located at the apices. Thallium ions are situated in the prismatic voids of the crystal structure of TlFeS$_2$ (or TlFeSe$_2$). The tetrahedra are connected to linear chains and are parallel to the base $c$ axis. Under normal conditions the unit-cell parameters have the values $a = 11.636$ Å, $b = 5.304$ Å, $c = 6.799$ Å and $\beta = 116.7^\circ$ in TlFeS$_2$; in TlFeSe$_2$ $a = 11.973$ Å, $b = 5.490$ Å, $c = 7.110$ Å and $\beta = 118.2^\circ$ [6, 7].

Recently, it was found that the phase transitions to the antiferromagnetic phase are observed at a temperature of $T \sim 190$ K in TlFeS$_2$ and in TlFeSe$_2$ at $T \sim 290$ K [8, 9].

To determine the mechanism of magnetic ordering in TlFeS$_2$ and TlFeSe$_2$ under the influence of low temperatures and to develop theoretical models of the antiferromagnet-paramagnet phase transition, information is required about the temperature behavior of the structural parameters at low temperatures. In this work the neutron diffraction study of TlFeS$_2$ and TlFeSe$_2$ is performed using the method of powder diffractometry within the temperature range of 10–320 K.

EXPERIMENTAL

TlFeS$_2$ and TlFeSe$_2$ crystals were synthesized by fusing particularly pure components (Ti, Fe, S and Se) taken in the stoichiometric ratios in quartz cells evacuated to $10^{-3}$ Pa. The reaction between the components took place during the process of synthesis starting from 673–723 K. The cell with the compound rotating around the axis was gradually (over 7–8 h) inserted into the hotter zone of the furnace at a rate of 1.5–3.0 cm/h and after exposure to a temperature of 1023 K for around 1–2 h it was slowly (5–6 h) cooled to room temperature. The TlFeS$_2$ and TlFeSe$_2$ compounds synthesized in this manner were single-phase.
Coordinates of atom and interatomic distances (monoclinic \(C2/m\) phase) in TlFeS\(_2\) and TlFeSe\(_2\) compounds at room temperature

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
<th>Interatomic distances, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TlFeS(_2) (C2/m, Z = 4)</td>
<td>Tl</td>
<td>0.330(2)</td>
<td>0</td>
<td>0.361(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0.254(1)</td>
<td>0</td>
<td>Fe–Fe (–(x, 1 – y, –z))</td>
</tr>
<tr>
<td>S1</td>
<td>0.041(1)</td>
<td>0</td>
<td>0.291(9)</td>
<td>Fe–S1 (–(x, y, –z))</td>
</tr>
<tr>
<td>(\beta = 116.7(4)^\circ) S2</td>
<td>0.717(7)</td>
<td>0</td>
<td>0.120(7)</td>
<td>Fe–S2 (0.5 + (x, 0.5 + y, z))</td>
</tr>
<tr>
<td>TlFeSe(_2) (C2/m, Z = 4)</td>
<td>Tl</td>
<td>0.333(9)</td>
<td>0</td>
<td>0.367(2)</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0.262(6)</td>
<td>0</td>
<td>Fe–Fe (–(x, 1 – y, –z))</td>
</tr>
<tr>
<td>Se1</td>
<td>0.039(1)</td>
<td>0</td>
<td>0.288(6)</td>
<td>Fe–S1 (–(x, y, –z))</td>
</tr>
<tr>
<td>(\beta = 118.2(1)^\circ) Se2</td>
<td>0.685(8)</td>
<td>0</td>
<td>0.094(4)</td>
<td>Fe–S2 (0.5 + (x, 0.5 + y, z))</td>
</tr>
</tbody>
</table>

A more detailed description of the mode of single-crystal synthesis was given in [10].

The experiments on neutron diffraction were performed using a DN–2 diffractometer [11, 12] located on a high-intensity pulsed neutron source, an IBR-2 reactor (Frank Laboratory of Nuclear Physics, Joint Institute of Nuclear Research, Dubna) in the temperature range of 10–320 K. The diffraction spectra were measured at the scattering angle \(2\theta = 90.3^\circ\). The characteristic time of measurement of one spectrum was 12 h. To record diffraction spectra using the DN–2 diffractometer we used the time-of-flight method; the total neutron flux on the sample is \(-5 \times 10^8\ \text{n/cm}^2\ \text{s}\), the resolution \(\Delta d/d\) over the interplanar distance at the scattering angle \(2\theta = 90.3^\circ\) is close to 0.01.

Neutron diffraction data were processed by the Rietveld method using the program VMRIA [13].

RESULTS AND DISCUSSION

The neutron spectra of TlFeS\(_2\) and TlFeSe\(_2\) obtained at different temperatures are shown in Fig. 1. At room temperature they correspond to the monoclinic symmetry \(C2/m\). The unit-cell parameters calculated from the diffraction data under normal conditions for TlFeS\(_2\) are \(a = 11.646(1)\ \text{Å}, b = 5.308(2)\ \text{Å}, c = 6.831(3)\ \text{Å}, \beta = 116.7(4)^\circ\); for TlFeSe\(_2\) they are \(a = 11.998(1)\ \text{Å}, b = 5.498(9)\ \text{Å}, c = 7.108(8)\ \text{Å}, \beta = 118.2(1)^\circ\), which is in agreement with the results of [8, 9]. In low-temperature experiments the antiferromagnet–paramagnet phase transition can be recorded by the appearance of new peaks \(21\frac{1}{2}T\) at \(d_{hkl} \sim 4\ \text{Å}\) and \(01\frac{1}{2}T\) at \(d_{hkl} \sim 5\ \text{Å}\) (Fig. 1).

The temperature dependences of the unit-cell parameters of TlFeS\(_2\) are shown in Fig. 2a. Linear functions were used during interpolation in the temperature range of 10–300 K. The linear thermal-expansion coefficients along the crystallographic directions \(k_i = (1/a_0)(da/dT)_p\) (\(a = a, b, c\)) are \(k_a = 3.70(5) \times 10^{-5}\ \text{K}^{-1}\), \(k_b = 1.43(3) \times 10^{-4}\ \text{K}^{-1}\) and \(k_c = 2.86(3) \times 10^{-5}\ \text{K}^{-1}\). Unlike the linear temperature dependence of parameters \(a, b\) and \(c\), the monoclinicity angle varies stepwise during the magnetic-phase transition. It is seen from Fig. 2b that the angle \(\beta\) increases with a decrease in temperature. The temperature dependence of the unit-cell volume of TlFeS\(_2\) is shown in Fig. 2c. The dependence of the unit-cell volume for each phase has a linear character. The volumetric thermal-expansion coefficient \(\alpha = 1/V(dV/dT)_p\) for the paramagnetic phase was \(\alpha = 6.28(1) \times 10^{-5}\ \text{K}^{-1}\), for the antiferromagnetic phase, it was \(\alpha = 2.65(6) \times 10^{-4}\ \text{K}^{-1}\).

The temperature dependences of the unit-cell parameters of TlFeSe\(_2\) are shown in Fig. 3a. Linear functions were used during interpolation in the temperature range of 10–320 K. The linear thermal-expansion coefficients along the crystallographic directions \(k_i = (1/a_0)(da/dT)_p\) (\(a = a, b, c\)) are \(k_a = 6.13(2) \times 10^{-5}\ \text{K}^{-1}\), \(k_b = 1.32(1) \times 10^{-4}\ \text{K}^{-1}\) and \(k_c = 5.86(4) \times 10^{-5}\ \text{K}^{-1}\). In this compound, the same as in the case of TlFeS\(_2\), unlike the \(a, b\) and \(c\) parameters, a sharp kink is observed in the temperature dependence of the angle \(\beta\) at the point of the magnetic-phase transition. It is seen in Fig. 3b that the angle \(\beta\) decreases with decreasing temperature. The temperature depen-