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THERMOPHYSICAL PROPERTIES OF $TlInTe_2$

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We present results of an investigation of the temperature dependences of the thermal expansion at different rates of heating and of the isothermal compressibility and the specific heat of $TlInTe_2$. The thermal and elastic parameters of the indicated phase have been determined.

The compound $TlInTe_2$ crystallizes in a TlSe-type structure. Thallium ions in $TlInTe_2$ have an octahedral environment, whereas its semiconductor properties are determined by trivalent indium ions with a covalent tetrahedral coordination. The compound $TlInTe_2$ crystallizes in a tetragonal syngony and has a space group of symmetry D_{4h}^{18} (I 4/mcm) with the lattice parameters a = 8.38 Å and c = 7.16 Å.

From the interpretation of the crystalline structure it is established that $TlInTe_2$ belongs to TlSe-type compounds. For $TlInTe_2$ the bond length in the tetrahedron is 2.56 Å, which, actually, turns out to be close to the sum of the covalent radii of indium and tellurium (2.79 Å), while the distance between the thallium and tellurium atoms (3.6 Å) in the octavertex corresponds to the sum of the ionic radii of tellurium and univalent thallium.

The electrophysical and photoelectric properties of $TlInTe_2$ have been investigated rather comprehensively in [1]. In particular, the forbidden gap of the indicated phase was determined from the temperature dependences of the electrical conductivity, the Hall coefficient, the photoconductivity, and the optical absorption. These data do not differ considerably. In [2], the electronic energy spectrum of $TlInTe_2$ is calculated by the pseudopotential method with the use of an analytical expression for atomic pseudopotentials. It is found that the compounds $TlInTe_2$ have a direct-band-gap structure. According to selection rules, direct transition of the electrons from the valence band to the conduction band is forbidden. The numerical values of the minimum direct and indirect gaps for $TlInTe_2$ are as follows: $E_{\mathrm{g}}^{\mathrm{dir}}$ = 1.16 eV and $E_{\mathrm{g}}^{\mathrm{ind}}$ = 0.65 eV. The analysis of the characteristic properties of the $TlInTe_2$ band structure showed the presence of an isolated group of four bands separated from the main group of valence bands by a wide gap of the order of 10 eV. The method of linear combinations of atomic orbitals points to the fact that these bands result in the main from the *s*-states of the tellurium atoms, whereas the valence-band top is formed by the *s*-states of the Tl atoms and by the *p*-states of the Te atoms. Consequently, the atoms with octahedral coordination (Tl) are of considerable importance in forming the semiconductor compound $TlInTe_2$.

Thus, the electrophysical and photoelectric properties of $TlInTe_2$ have been studied in sufficient detail. The aim of the present work is to investigate the thermophysical properties of $TlInTe_2$. In particular, we consider the temperature dependences of the coefficient of thermal expansion (CTE), the isothermal compressibility (IC), and the specific heat of $TlInTe_2$ and determine the thermal and elastic parameters of the indicated phase.

The coefficient of thermal expansion and the isothermal compressibility were investigated in the temperature range 4.2–400 K on the setup described in [3]. The measurement error for the standard specimens made of aluminum and copper was 3 and 4% respectively. The order of the investigations was as follows: to heat a cylindrical specimen of diameter 0.005 m and length 0.02 m throughout its length we bifilarly coiled a constantan wire (coil with coil closed together) of diameter 10^{-4} m with silk insulation and then coated the coiling surface with a thin layer of BF-2 adhesive, thus favoring a smooth and uniform change in the temperature of all the portions of the specimen. The specimen temperature was measured by a copper-constantan thermocouple. For the reliability of measurements, we used three pairs of thermocouples which were glued to the upper, middle, and lower portions of the specimen.

The results of measurements of the coefficient of thermal expansion of $TlInTe_2$ as a function of the temperature are presented in Fig. 1.

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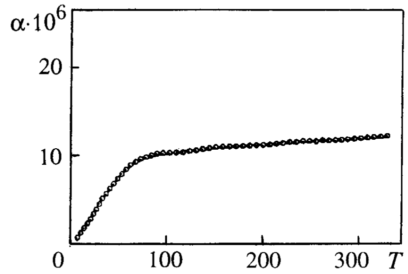


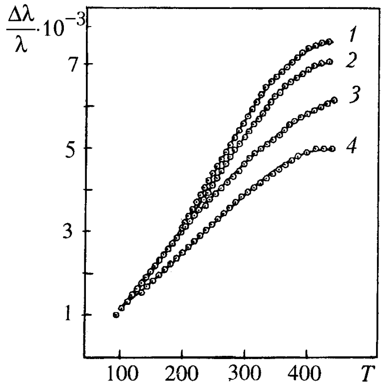
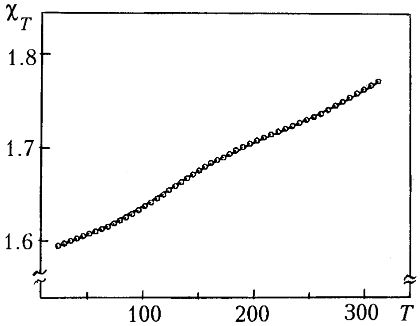


Fig. 1. Temperature dependence of the thermal expansion of $TlInTe_2$.

Fig. 2. Temperature dependence of the relative elongation of $TlInTe_2$ at different rates of heating: 1) 3, 2) 2.4, 3) 2.0, and 4) 1.6 K/min.



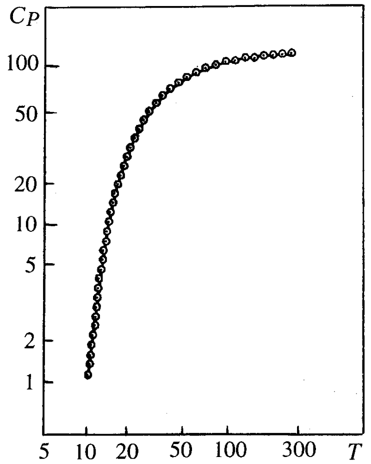


Fig. 3. Temperature dependence of the isothermal compressibility of $TlInTe_2$.

Fig. 4. Temperature dependence of the specific heat of $TlInTe_2$.

As follows from this figure, at low temperatures the coefficient of thermal expansion increases heavily. This seems to be associated with the fact that in the unit cell of $TlInTe_2$ the thallium and indium atoms occupy two crystallographically independent positions. The formula of $TlInTe_2$ can be written in the form $Tl^+(In^{3+}Te_2^-)^-$. Here Tl^+ remains in the octahedral environment of the tellurium atoms, while the cations of trivalent indium In^{3+} remain in the tetrahedral environment of the univalent-thallium atoms. The greatest expansion is observed in the direction of weak bonds, i.e., a sharp increase in the coefficient of thermal expansion occurs probably in the direction of weak bonds. The weak bonds in $TlInTe_2$ are spaced between the chains $(In^{3+}Te_2^-)^-$. At temperatures above 280 K, the increase in the coefficient of thermal expansion becomes insignificant.

We investigated the relative elongation (RE) of $TlInTe_2$ as a function of the rate of heating. From Fig. 2 it follows that at low temperatures, irrespective of the heating rate, the relative elongation is identical for $TlInTe_2$ and it increases monotonically with rise in the temperature. Beginning at 240 K, as the heating rate decreases, the relative elongation increases. This seems to be attributed to the fact that with change in the external factors, in particular, the temperature, one observes a "devil’s staircase" in structures of the TlSe-type [4]. Here, the system successively experiences a large number of intermediate states. The presence of defects and quantum and thermal fluctuations changes the "devil’s staircase" into a harmless one, making the number of admissible comparable states infinite.

Using the Maxwell relation

$$\rho_{ik} = \frac{\partial U_{ik}}{\partial T},$$

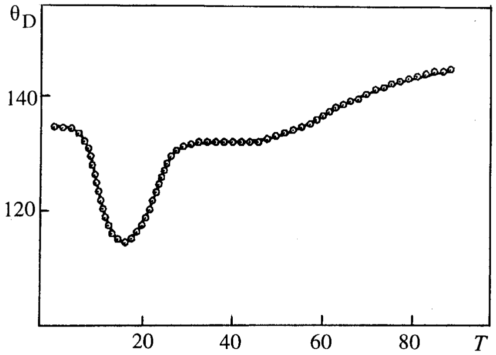


Fig. 5. Temperature dependence of the Debye temperature of $TlInTe_2$.

we can easily infer that the anomalies observed in thermal expansion can be explained by the rearrangement of the crystalline structure of $TlInTe_2$. Indeed, with change in the temperature, the crystal length changes in the direction of the **c** axis, since the rigid sublattice is deformed precisely in the direction of the **c** axis.

The dependence of the thermal expansion on the heating rate is determined by the presence of a large number of competing phases with close free energies separated from each other by potential barriers.

Figure 3 gives the temperature dependence of the isothermal compressibility of $TlInTe_2$. It is found that the isothermal compressibility increases throughout the temperature range with rise in the temperature.

We investigated the specific heat of $TlInTe_2$ in the temperature range 4.2–350 K on the setup described in [5]. The experimental results are given in Fig. 4. As is seen, the specific heat increases monotonically, and its anomalies, just as those of the coefficient of thermal expansion and the isothermal compressibility, are not revealed. The analysis of the results obtained has shown that the Debye cubic law for $TlInTe_2$ is not obeyed in the investigated temperature range. The change in the specific heat in the temperature range from 14 to 42 K occurs following the law $C = a + bT$, where $a = -12.5$ J/(mole·K) and $b = 1.93$ J/(mole·K^2); this is probably caused by the main contribution of the transverse branch of the phonon spectrum to the specific heat [5], which at constant volume (C_V), can be found from the relation

$$C_V = C_P - \frac{\beta^2 VT}{\chi_T}, \quad \beta = 3 .$$

At a temperature above 135 K, the specific heat of $TlInTe_2$ exceeds its classical value and is temperature dependent in connection with the anharmonicity of the lattice vibrations. From the relation

$$\frac{C_V - 3R}{T} = f\left(\frac{1}{T^3}\right)$$

we determined the anharmonic component $C_V = 1.4 \cdot 10^{-8} T$. The Grüneisen parameter is found using the formula

$$\gamma = \frac{\beta V}{\chi_T C_V} .$$

It is found that the parameter γ strongly depends on the temperature (to 90 K), and at room temperature it is equal to 1.35. In the range 5–90 K, we calculated the Debye temperature by means of $C_V(T)$ and established that to 14 K it decreases. This is probably associated with a soft optical mode which is manifested due to the weak interaction between the chains and increases gradually with rise in the temperature θ_D (Fig. 5).

Using the data of the specific heat, we calculated the entropy, enthalpy, and Gibbs free reduced energy from the formulas [6]

TABLE 1. Thermal and Elastic Parameters of the Compound $TlInTe_2$

T	C_P	ΔS	ΔH	ΔF
20	27.752	4.31	$15.5\cdot10^{-3}$	–5.697
30	54.372	20.505	$56.3\cdot10^{-3}$	–22.317
40	84.559	40.253	$1258\cdot10^{-3}$	–42.392
50	126.24	63.496	$2307\cdot10^{-3}$	–66.021
60	179.796	91.042	$3826\cdot10^{-3}$	–94.038
70	246.419	123.6	$5947\cdot10^{-3}$	–127.12
80	325.612	161.526	$8796\cdot10^{-3}$	–165.596
90	422.838	205.247	$12.52\cdot10^{-3}$	–261.992
100	560.321	256.389	$17.38\cdot10^{-3}$	–261.992

$$S_T - S_0 = \int_0^T \frac{C_P(T)}{T}\, dT\,,$$

$$H_T - H_0 = \int_0^T C_P(T)\, dT\,,$$

$$\Delta F = -\left(S_T - \frac{H_T - H_0}{T}\right).$$

The results of calculations of the thermal and elastic parameters are presented in Table 1.

Thus, based on the investigation of the temperature dependences of the thermal expansion at different heating rates and of the isothermal compressibility and the specific heat of the compound $TlInTe_2$, we have determined the thermal and elastic parameters of this compound.

NOTATION

C_V, specific heat at constant volume, J/(mole·K); C_P, specific heat at constant pressure, J/(mole·K); ΔS, change in the entropy, J/(mole·K); ΔH, change in the enthalpy, J/mole; ΔF, Gibbs free reduced energy, J/(mole·K); β, coefficient of volumetric thermal expansion, K^{-1}; χ_T, isothermal compressibility, m^2/N; T, absolute temperature, K; V, molar volume, m^3; γ, Grüneisen parameter; θ_D, Debye temperature, K; ρ_{ik}, change in the potential energy with temperature, J/K; U_{ik}, potential energy of the lattice, J; E, transition energy, eV; a and c, parameters of the unit cell, Å; D_{2h}^{18} (I 4/mcm), symbol of the space group of symmetry of the tetragonal syngony. Subscripts: i and k, numbers of quantum and thermal fluctuations; D, Debye; g, range; dir, direct; ind, indirect.

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