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SPECIFIC HEATS OF THALLIUM SULFIDE, SELENIDE, AND TELLURIDE AT LOW TEMPERATURES

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UDC 548.536

Specific heats of TlX (X = S, Se, and Te) semiconductor crystals were studied at low temperatures. The Debye temperatures and the thermodynamic parameters of these compounds were determined.

The physical properties of type $A^{III}B^{VI}$ (A = Ga, In, Tl; B = S, Se, Te) semiconductor compounds have been studied intensively in the last few years. These crystals are strongly anisotropic, and various semiconductor devices based on them have been produced — lasers, memory elements, switching mechanisms, etc. The operating conditions of these devices are determined largely by the thermal characteristics of the crystal employed. On the other hand, the study of thermal properties, in particular the specific heat, is of great interest for the development of crystal physics.

The specific heats of certain representative semiconductors of the $A^{III}B^{VI}$ type were studied at low temperatures in [1, 2].

Samples of TlX (X = S, Se, Te) were obtained by vacuum ($1.33\cdot10^{-2}$ N/m^2) melting of the elementary components in a stoichiometric ratio with subsequent annealing of the compounds formed to homogenize them. An x-ray analysis showed single-phase samples were present; the tetragonal lattice constants at room temperature were: $a = 7.75$, $c = 6.80$; $a = 8.03$, $c = 7.00$; $a = 12.96$, $c = 6.18$ Å, respectively, for TlS, TlSe, and TlTe, and are in good agreement with values in [3, 4].

It should be noted that the thallium monochalcogenides we studied have a tetragonal lattice structure. However, a study [5] of the TlTe structure showed that the spatial distribution of atoms in a unit cell of TlTe is significantly different from that in TlS and TlSe.

The specific heats of TlX (S = S, Se, Te) crystals were measured with the arrangement described in [6]. Adiabatic conditions were maintained by automatic precision temperature controls of the PRT-2M type. The temperature of the calorimeter was measured with TSG-2, and TSPN-2B germanium and platinum resistance thermometers. The error of the measurements below 4°K was estimated as 5% or less, and above 5°K as 1.5-0.2%.

The experimental values of the specific heats of TlX (X = S, Se, Te) compounds are shown in Fig. 1 together with earlier data [7, 8] and data from [9]. The smoothed-out values of $C_p(T)$ are listed in Table 1.

Institute of Physics, Academy of Sciences of the Azerbaidzhan SSR, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 39, No. 6, pp. 1005-1009, December, 1980. Original article submitted June 28, 1979.

0022-0841/80/3906-1310\$07.50

TABLE 1. Smoothed-Out Values of the Specific Heat of Thallium Sulfide, Selenide, and Telluride

T, °K	c_p, J/kg·deg			T, °K	c_p, J/kg·deg		
	TlS	TlSe	TlTe		TlS	TlSe	TlTe
2	0,142	0,162	0,227	110	167,1	153,2	145,2
3	0,407	0,458	0,643	120	172,9	156,4	147,2
5	1,73	1,90	2,45	130	176,8	159,1	149,2
7	4,69	5,99	5,88	140	180,0	161,4	150,6
10	10,49	12,85	15,99	150	182,5	163,2	151,7
15	34,5	32,5	33,4	160	185,0	164,8	152,5
20	52,1	46,6	55,1	170	187,6	166,3	152,6
30	79,4	71,5	84,2	180	190,3	167,9	153,5
40	98,2	89,5	106,4	190	192,8	169,4	153,7
50	112,9	105,7	117,6	200	194,7	170,5	154,1
60	126,0	119,2	126,3	220	198,2	171,5	155,0
70	138,4	129,4	133,5	240	201,3	172,2	156,1
80	148,1	137,7	137,8	260	204,1	173,5	157,5
90	155,1	144,1	140,5	280	207,1	174,7	158,6
100	161,1	149,2	143,0	300	210,1	176,5	159,9

Studies show that the Debye T^3 law is obeyed for thallium monochalcogenides below helium temperatures. The molar heat capacity of the compounds studied below 3.7, 3.3, and 3.0°K, respectively, for TlS, TlSe, and TlTe are given by the expression

$$C_v = \frac{12}{5}\pi^4 R n_0 \left(\frac{T}{\theta_0}\right)^3, \tag{1}$$

θ_0 turned out to be 106.0 ± 0.5, 94 ± 1, and 79 ± 1°K for TlS, TlSe, and TlTe, respectively.

The TlX (X = S, Se, Te) crystals are anisotropic with respect to elastic properties. Data on these properties, in particular for TlS and TlSe, are given in [10, 11].

The temperature dependence of the Debye temperature $\theta_D(T)$ for TlX (X = S, Se, Te), calculated from the low-temperature specific heats, is shown in Fig. 2. The curves for $\theta_D(T)$ show that above 4°K the specific heat of the crystals mentioned do not follow the Debye specific heat law

$$C_v = 3Rn_0 D\left(\frac{\theta_0}{T}\right). \tag{2}$$

Figure 1 shows that in the range 6-20°K the data from [9] on TlSe are in satisfactory agreement with our results, but below 6°K they diverge beyond the limits of experimental error, and the difference increases with decreasing temperature. Figure 2 also shows the Debye temperature of TlSe calculated from the data in [9]. We note that below 6°K the values of $\theta_D(T)$ increase sharply, and at 3°K reach values of 142°K. Such a sharp increase in $\theta_D(T)$ over a narrow temperature range obviously cannot be expected, even taking account of the fact that the sample used in [9] was a single crystal.

On the $C_p(T)$ curve for TlTe there is observed for the first time an anomaly in a narrow temperature range (~7°K) in the neighborhood of 170°K, where the specific heat increases sharply (by almost 50%) and at T_t = 171.80°K passes through a maximum. The phase transition in TlTe is observed also on curves of the electrical conductivity, thermoelectromotive force, the Hall effect, and on diffraction patterns taken at 80 and 300°K [12]. Taking account of the behavior of the specific heat near the transition temperature, and the absence of latent heat, it can be assumed that the observed transition in TlTe is a phase transition of the second kind [12, 13].

TABLE 2. Standard Values of the Specific Heat, Entropy, Enthalpy, and Gibbs Reduced Energy of Thallium Sulfide, Selenide, and Telluride at T = 298.15°K

Compound	c_p, J/kg·deg	S_T^0, J/kg·deg	$(H_T-H_0)\cdot 10^{-3}$, J/kg	$-(F_T-F_9)$ J/kg·deg
TlS	209,9	407±2	48,5±0,1	244 ±1
TlSe	176,2	362∓1	42,2∓0,1	222 ±1
TlTe	159,8	372∓1	40,5∓0,1	236 ±1

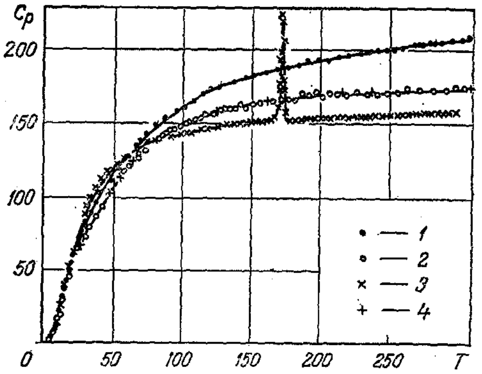

Fig. 1

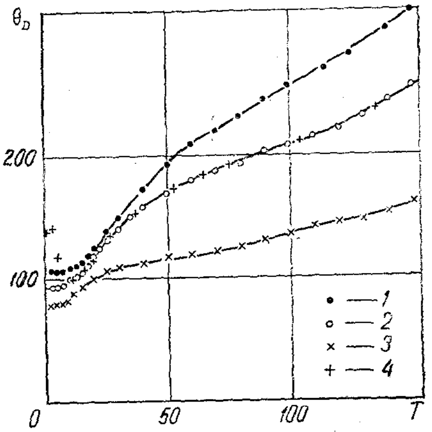

Fig. 2

Fig. 1. Temperature dependence of specific heat (J/kg· deg) of thallium sulfide, selenide, and telluride. 1) TlS; 2) TlSe; 3) TlTe; 4) data from [9]. T in °K.

Fig. 2. θ_D as a function of T for thallium sulfide, selenide, and telluride. 1) TlS; 2) TlSe; 3) TlTe; 4) data from [9]. θ_D in °K.

Analysis of the results obtained for the specific heats of TlS, TlSe, and TlTe (the first two clearly have a chain structure) shows that there is no rather broad range of temperatures where the behavior of the specific heat is described by the limiting laws of the specific heat of chain crystals. Nevertheless, the behavior of the specific heat curves for TlS and TlSe is closer to that predicted by the theory of Lifshitz [14] than to the conclusions in [15]. Thus, e.g., for TlS in the range 62-85°K we have $C_V \sim T^{0.54}$, and for T*l*Se in the range 60-87°K $C_V \sim T^{0.44}$, which is close to the $C_V \sim T^{1/2}$ law.

We note that the specific heat of TlTe obeys a linear law in the range 20-40°K. This behavior of the specific heat is apparently related to the characteristics of the TlTe structure [5], which is close to two-dimensional.

The experimental data show that the Debye temperature θ_0, the melting point T_{me}, and the molecular weight M of TlX (X = S, Se, Te) crystals are correlated. It has been established that θ_0 and M for the crystals mentioned are related by a linear law of the form $\theta_0 = a - bM$, with a and b equal to 172.5 and 0.28, respectively. It is interesting to note that for GaX (X = S, Se, Te) these parameters are inversely proportional [6].

The experimental results for the specific heat $C_p(T)$ in the range 2-300°K were used to calculate the principal thermodynamic parameters — entropy S_T^0, change in enthalpy $H_T - H_0$, and Gibbs reduced energy $[-(S_T - (H_T - H_0)/T)]$ — of TlX (X = S, Se, Te) crystals. The standard values of these quantities are listed in Table 2.

NOTATION

T, temperature; T_{me}, melting point; C_p, specific heat at constant pressure; C_V, specific heat at constant volume; R, universal gas constant; n_0, number of atoms per molecule, $\theta_0 = h\omega_{max}/k$, characteristic Debye temperature as T → 0°K; h, Planck's constant; ω_{max}, maximum frequency; k, Boltzmann's constant; θ_D, effective Debye temperature; $D(\theta_0/T)$, Debye specific heat function; T_t, transition temperature; M, molecular weight; S_T^0, entropy; $H_T - H_0$, change in enthalpy; $F_T - F_0$, Gibbs reduced energy.

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