$$\frac{\Delta\varphi - \Delta T(t)}{\Delta\varphi} = \frac{4}{\sqrt{\pi} b} \sqrt{kt} + O((kt)^{3/2}). \tag{26}$$

Therefore, measurement of the nonstationary superposed effects considered permits the determination [formulas (11) and (26)] of the coefficient of thermal diffusivity k, and therefore, also of the heat-conduction coefficient λ for known c (specific heat) and ρ (density), as well as the thermal fluxes of the effects w_E, w_{RL}, w_N, w_P, w_{MRL} [formula (6) and its variants (12), (14), (16), (24)].

Under certain conditions several (usually two) of the superposed effects can be registered simultaneously on the measurement probes in the experiment. In these cases (26) and (11) retain their form; just Δφ therein has the meaning of a total (complete) stationary temperature drop. Therefore, the simultaneous measurement of the superposed effects does not hinder the determination of k and λ. Further investigations in this area should concern the explanation of nature and formulas for the additional heat fluxes of the effects w_E, w_{RL}, etc.

The analysis performed on the possibilities of determining the thermophysical properties of semiconductors substantially expands the prospects for using the method of variation of the AF in experimental investigations. The results obtained can turn out to be useful in studying the physical properties of thin films of solid materials and compounds, as well as in rheological investigations of different fluid media.

NOTATION

T_m, temperature of the surrounding medium; j, current density; w, heat flux of the different effects; σ, λ, k, α, a, coefficients of electrical, thermal conductivity, thermal diffusivity, thermal emf, and heat exchange with the surrounding medium; d, perimeter of the specimen cross section, and Δφ, initial temperature difference in the specimen.

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LATTICE THERMAL CONDUCTIVITY AND CHEMICAL BOND IN THE HYPOVALENT TWO-CATION SEMICONDUCTORS $A^1SbC_2^6$ AND $TlB^5C_2^6$

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The relation between the lattice thermal conductivity of $A^1SbC_2^6$ (A^1 = Li, Na, K, Rb, Cs; C^6 = S, Se) and $TlB^5C_2^6$ (B^5 = As, Sb, Bi; C_2^6 = S, Se, Te) and the nature of the chemical bond is investigated. It is shown that the relative radii of the atoms affects the melting point and thermal conductivity of these compounds.

The lattice thermal conductivity of complex semiconductors depends significantly on the chemical composition, structure, and nature of the chemical bond [1, 2]. The two groups of compounds that we selected as objects of investigation are largely analogous. Compounds of both groups are hypovalent chalcogenide semiconductors, since the B^5 elements are trivalent, and Tl in the second group of compounds is monovalent. They are formed in analogous quasi-binary sections A_2^1—$B_2^5C_3^6$ and Tl_2C^6—$B_2^5C_3^6$ with an equimolar ratio of the binary components [4-7].

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TABLE 1. Some Physicochemical Characteristics of Compounds $A^1SbC_2^6$ and $TlB^5C_2^6$

№	Compound	$\bar{A}$	$T_{m.e}$	$T_{m.c}$	Θ	$\varkappa_{l.e}$	$\varkappa_{l.c}$	n	R	i_l	i_π
1	$LiSbS_2$	48,2	940	929	228	4	0,80	0,84	1,51	27	24
2	$NaSbS_2$	52,2	1010	856	218	3,3	2,22	0,85	1,61	30	27
3	$KSbS_2$	56,2	783	685	168	1,58	1,93	0,85	1,78	30	28
4	$RbSbS_2$	67,7	733	636	151	1,10	1,60	0,86	1,82	34	28
5	$CsSbS_2$	79,7	673	611	127	0,73	1,20	0,87	1,83	38	30
6	$NaSbSe_2$	75,6	1013	782	174	2,25	1,40	0,83	1,68	25	21
7	$KSbSe_2$	77,2	733	763	145	1,05	1,31	0,845	1,84	28	25
8	$TlAsS_2$	85,8	578	676	140	0,95	0,62	0,91	1,77	38	18
9	$TlAsSe_2$	109,3	538	628	105	0,85	0,61	0,80	1,83	22	12
10	$TlAsTe_2$	133,6	573	507	85	0,70	0,72	0,68	1,94	12	4
11	$TlSbS_2$	97,5	733	941	133	1,10	1,36	0,85	1,48	30	22
12	$TlSbSe_2$	128,5	753	869	110	0,94	1,22	0,79	1,54	18	15
13	$TlSbTe_2$	145,3	753	797	100	0,88	1,13	0,75	1,64	15	6
14	$TlBiS_2$	119,4	1013	1086	130	1,20	1,89	0,85	1,29	30	25
15	$TlBiSe_2$	142,8	983	1038	110	1,05	1,82	0,79	1,34	18	16
16	$TlBiTe_2$	161,1	808	989	96	1,00	2,38	0,64	1,45	10	10

Compounds of the $A^1SbC_2^6$ group are high-resistance broad-band semiconductors with hole conductivity. They are characterized by an unusual feature — the increase in energy gap width on transition to compounds with heavier alkaline elements accompanied by a reduction of melting point and microhardness [8, 9]. A similar situation is observed in the related compounds $A^1As(Bi)C_2^6$ [10].

The ternary compounds $TlB^5C_2^6$, like the compounds $A^1B^5C_2^6$, are characterized by a mixed ionic—covalent type of chemical bond with some measure of metallization. The latter increases with the changes As → Sb → Bi, S → Se → Te [11-13]. The difference in electronegativity and, hence, the degree of ionicity of the chemical bond, however, is lower in them than in the compounds $A^1B^5C_2^6$. Nevertheless, the two groups of compounds under consideration can be assigned to the same class of ternary semiconductors since, in accordance with the chemical analogy principle [14], they show a similarity in the mode of formation of the valence bonds, in the chemical composition of the anions and cations, the type of valence, and in the mean valence electron concentration.

The first experimental investigations of the thermal conductivity of the compounds $A^1SbC_2^6$ and $TlB^5C_2^6$ [3, 9, 15] showed that the effect of the nature of the chemical bond on the thermal conductivity and its temperature dependence is of a complex nature and the explanation of the discovered relations requires a consideration not only of the specificity of the crystalline structure but also of the electronic configuration of the atoms.

The experimental procedure is described in [3, 9, 15]. For the compounds under consideration Table 1 gives data on the mean atomic mass $\bar{A}$, the experimentally determined melting point $T_{m.e}$, the melting point calculated from Eq. (3) ($T_{m.c}$), the Debye temperature Θ the lattice thermal conductivity at 300°K, determined experimentally ($\varkappa_{l.e}$) and calculated from Eq. (4) ($\varkappa_{l.c}$), the exponent n in Eq. (4), the relative radius R, the degree of ionicity of the chemical band, determined from the relation between the lattice thermal conductivity and the mean atomic mass (i_l) and calculated by Pauling's method (i_π) [18].

With increase in the mean atomic mass of the compounds $A^1SbC_2^6$ the lattice thermal conductivity decreases with the changes Na → K → Rb → Cs and with the change S → Se. In compounds $TlB^5C_2^6$ the lattice thermal conductivity decreases with increase in the mean atomic mass due to the changes S → Se → Te, whereas with the changes As → Sb → Bi it increases. This regular variation of $\varkappa_l$ with change in the mean atomic mass in the investigated groups of crystalline compounds (apart from $LiSbS_2$, $LiSbSe_2$ [3]) occurs in the temperature range 80-300°K.

X-ray structural investigations showed that with increase in the atomic number of the alkaline element, and also on changeover from sulfides to selenides in compounds $A^1SbC_2^6$, the symmetry of the crystal lattice is reduced and there is an increasing tendency to loosening of the structure due to increase in the concentration of point defects, among which cationic vacancies predominate.

The lattice thermal conductivity of semiconductors has a temperature dependence $\varkappa(T)$ with a maximum at $T < \Theta$ [2]. At temperatures $T > \Theta$ the decisive heat-transfer processes are

Umklapp processes. It should be pointed out that even for perfect crystals the theory of lattice thermal conductivity at $T > \Theta$ has not been so well developed as for low temperatures. Peierls [16] established that at high temperatures

$$\varkappa_l \sim \frac{\Theta}{T}. \tag{1}$$

This relation is strict and is well confirmed by numerous experiments. The appropriate proportionality constants have to be found empirically for numerical calculations for different groups of crystalline semiconductors.

The dependence of the lattice thermal conductivity on the type of chemical bond and the mean atomic mass, as exemplified by several groups of binary semiconductors, was investigated by Ioffe [1, 17, 19], who found a regular reduction of $\varkappa_l$ with increase in the mean atomic mass and also with changeover from covalent to ionic compounds.

An analysis of the experimental results given in Table 1 shows that such a reduction of $\varkappa_l$ is also observed in the investigated ternary compounds. It is probably of a general nature [11].

The dependence of $\varkappa_l$ on the mean atomic mass, structure, and type of chemical bond indicates a significant role of the ratio of the ionic and covalent radii of the elements forming the compounds. It is known, for instance, that the ratio of the radius of the anion to the radius of the cation has a significant effect on the melting point [18]. Bazakutsa et al. [9] showed that the energy gap width, the thermo-emf coefficient, and the specific electrical conductivity of $A^1SbS_2(Se_2)$ depend on the ionic radii of the alkaline elements.

As a dimensionless parameter taking into account the ionic and covalent radii of the compounds we took the ratio

$$R = \frac{(R_A + R_C)_c(R_A + R_C)_i}{(R_B + R_C)_c(R_A + R_B)_i}, \tag{2}$$

in which R_A, R_B, and R_C are the covalent or ionic radii of the elements (the subscript c indicates covalent, and i ionic).

The establishment of correlations between R and other parameters characterizing the compounds is mathematically analogous to the solution of the problem of optimal design of experiments. Hence, for this purpose we used the methods of least squares and multifactorial regression analysis [21-23]. Computer calculations were made with the aid of an appropriate standard program.

The results of a multifactorial correlation analysis for the two groups of considered compounds showed that for them the relation between the melting point $T_{m.c}$ and R is given by the equation

$$T_{m.c} = 2.414\cdot 10^3\left(\frac{1}{R + \frac{1}{R}} - 1\right)K. \tag{3}$$

The mean deviation of the experimental data for $T_{m.e}$ from the calculated data was 13.6%, and the maximum deviation for individual compounds did not exceed 29%. In view of the relatively low accuracy of the values of the ionic and covalent radii [18] determining R we can establish a good correlation between T_m and R and, hence, a satisfactory representation by Eq. (3) of the dependence of T_m on the structure and chemical composition of compounds of the investigated class.

The generality of the laws to which the compounds $A^1SbC_2^6$ and $TlB^5C_2^6$ conform was confirmed by an analysis of the changes in lattice thermal conductivity in these groups. On processing of the experimental data for these compounds on an M-222 computer we obtained a general formula

$$\varkappa_{l.c} = \frac{\rho^{0.3}\Theta^{0.75}T_{m.e}}{\bar{A}^n T}\left(\frac{3}{R + \frac{1}{R}} - 1\right)W/m\cdot{}^\circ K \tag{4}$$

where ρ is the density of the compounds; $T = 300^\circ K$; $T_{m.e}$ is the melting point (experimental value); $\bar{A}$ is the mean atomic mass of the compounds; Θ is the Debye temperature.

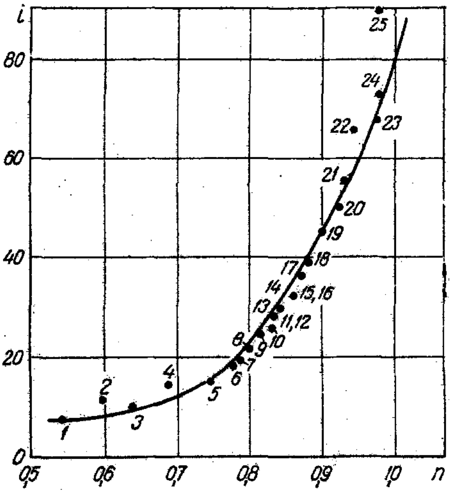

Fig. 1. Degree of ionicity (i, %) of chemical bond of compounds as function of exponent n: 1) AlSb [20]; 2) GaSb [20]; 3) $TlBiTe_2$; 4) $TlAsTe_2$; 5) $TlSbTe_2$; 6) $TlSbSe_2$; 7) $TlBiSe_2$; 8) $TlAsSe_2$; 9) $NaSbSe_2$; 10) $TlSbS_2$; 11) $KSbS_2$; 12) $TlBiS_2$; 13) $LiSbS_2$; 14) $NaSbS_2$; 15) $KSbSe_2$; 16) AlAs [20]; 17) $RbSbS_2$; 18) $CsSbS_2$; 19) $TlAsS_2$; 20) RbI [17, 19]; 21) NaBr [17, 19]; 22) RbBr [17, 19]; 23) NaCl [17, 19]; 24) KCl [17, 19]; 25) LiF [17, 19].

For the compounds $A^1B^5C^6_2$ the values of the exponent were obtained by analysis of the relation between $\ln \varkappa_{l.e}$ and $\ln \bar{A}$ [24]. The relation between the degree of ionicity i of the chemical bond and the exponent n was satisfactorily approximated by the equation

$$i = a\exp(bn), \tag{5}$$

where $a = 0.331$; $b = 5.3785$. The mean deviation of the calculated points from the experimental points did not exceed 10%.

The application of Eq. (5) to compounds of the $TlB^5C^6_2$ group led, as Table 1 shows, to a satisfactory agreement between the values of $\varkappa_{l.e}$ and $\varkappa_{l.c}$. The mean deviation of the experimental values of $\varkappa_{l.e}$ from the calculated values (excluding $LiSbS_2$ and $TlBiTe_2$) was 25%.

Figure 1 shows relation (5) in the form of a smooth curve, while the points correspond to the values of n calculated from Eq. (4) if $\varkappa_{l.c}$ is replaced by $\varkappa_{l.e}$. Figure 1 also shows published data for some binary compounds [17, 19, 20] with either a covalent or ionic component of the chemical bond. The correlation between n and i, shown in Fig. 1, indicates the universality of the relation $\varkappa_l \sim \bar{A}^n$ [1] and that relation (4) can be used to evaluate the degree of ionicity of the chemical bond of a wide circle of crystalline semiconductors from experimental values of the lattice thermal conductivity.

The increase in thermal conductivity of the compounds $TlB^5C^6_2$ with the changes As → Sb → Bi, which takes place in spite of the increase in mean atomic mass of the compounds, is easily explained, in correspondence with Eq. (4), by the reduction of the exponent n, i.e., reduction of the degree of ionicity of the chemical bond.

Thus, this investigation of the correlation between T_m and $\varkappa_l$, on one hand, and the degree of ionicity of the chemical bond, the mean atomic mass, and other parameters of the compounds $A^1B^5C^6_2$ and $TlB^5C^6_2$, on the other, confirms the common nature of these groups of complex semiconductors and allows an interpretation, from a common viewpoint, of the established dependence of the physical properties on the chemical composition and nature of the chemical bond.

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NOTATION

Θ, Debye temperature; $T_{m.e}$, experimental melting point, °K; $T_{m.c}$, calculated melting point, °K; $\bar{A}$, mean atomic mass of compound; $\varkappa_{l.e}$, experimental lattice conductivity, W/m·deg K; n, exponent of mean atomic mass; R, relative ionic radius; i_l, degree of ionicity of chemical bond determined from thermal conductivity; i_π, degree of ionicity of chemical bond determined by Pauling's method; T, temperature, °K; $(R_A, R_B, R_C)_c$, covalent radii of atoms A^I, B^5, C^6; $(R_A, R_B, R_C)_i$, ionic radii of atoms A^1, B^5, C^6; ρ, density of compound.

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AN EXPERIMENTAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF CYCLOHEXANE

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Measurements of thermal conductivity and specific heat of cyclohexane are presented for the temperature range 293-623°K for pressures of 2-30 MPa.

A knowledge of the thermophysical properties of liquids, foremost, specific heat and thermal conductivity, is necessary for study of the character of thermal molecular motion and transfer processes with the liquids [1, 2]. In recent years studies have demonstrated that in liquids which are semitransparent in infrared regions of the spectrum there exists together with a molecular heat-transfer mechanism a photon mechanism which has a marked effect even at room temperatures [3]. A consequence of this fact is that data on thermal conductivity of organic liquids are distorted in the majority of cases by a radiant component, the magnitude of which is difficult to estimate [3]. Under such conditions it is of interest to study the purely molecular thermal conductivity of liquids over a wide range of states and at high pressure singularities.

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