THERMAL CONDUCTIVITY OF TRIPLE SEMICONDUCTORS OF $A^1SbC^6_2$ TYPE AS A FUNCTION OF CHEMICAL COMPOSITION AND STRUCTURE

V. A. Bazakutsa and M. P. Vasil'eva

UDC 536.21

This paper studies the laws for variation of the thermal conductivity of incompletely valent chalcogenide compounds $A^1SbC^6_2$ (A^1 – Li, Na, K, Rb, Cs; C^6 – S, Se) as a function of their chemical composition and structure.

The recently synthesized incompletely valent triple chalcogenide compounds $A^1SbC^6_2$ are promising new semiconductor materials [1, 2]. The investigation of the thermal conductivity of these compounds as a function of chemical composition and structure is a matter of specific interest, from the viewpoint of explaining the systematic influence of variations in the nature of chemical bonds on the properties of complex semiconductors in the Li → Cs and S → Se transitions. The topical nature of this kind of investigation stems, on the one hand, from the fact that the thermal conductivity of triple semiconductors has generally received extremely little study [3], and additionally, because of the marked variations in the thermal conductivity and its temperature dependence with change in the dominant type of chemical bond [4]. The lattice component of the thermal conductivity of complex compounds is the most sensitive to the form of bond, and this has been expressed indirectly in formulating the dependence of thermal conductivity on the average atomic mass and coordinate number [5]. The low electrical conductivity of $A^1SbC^6_2$ [2, 6, 7] compounds stems from the fact that in the temperature range 80-350°K the lattice component of their thermal conductivity is practically the same as the total conductivity. This feature of the semiconductors studied makes it easy to analyze the influence of changes in the nature of the chemical bond and structure on the thermal conductivity, as the position of the component elements changes in the Mendeleev periodic system.

For the investigation we used specimens synthetized at the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of USSR (IONKh AN SSSR) by fusing elements and subsequently rendering them homogeneous [1, 8].

The specific thermal conductivity was measured on cast specimens of cylindrical form, of length 6-10 mm and diameter 6-8 mm, under steady-state thermal conditions of an apparatus which has been described in detail in [9]. The relative error of measurement did not exceed 8%.

All the specimens are semiconductors with p-type conductivity, whose electrical conductivity in the temperature range 80-300°K does not exceed 10^{-2} mho · m^{-1}.

The Debye temperatures were found from the temperature dependence of the specific heat (Fig. 1), determined by the method used in [10]. The values thus obtained for the Debye temperature Θ practically coincided with values calculated from the approximation

$$\Theta = CT_f^{1/2}\bar{A}^{-5/6}\rho^{1/3}, \tag{1}$$

found from the Lindeman fusion rule [11], in which C is a dimensionless constant, equal to 120.

All the compounds tested can be divided into three subgroups in regard to the nature of the temperature dependence of the thermal conductivity.

The first group contains the compounds $NaSbS_2$ (β-modification), $KSbS_2$ and $RbSbS_2$. The thermal conductivity of these substances in the temperature range studied is inversely proportional to temperature (Fig. 2a), which points to a phonon mechanism for heat dissipation with dominant three-phonon processes. The lattice thermal conductivity $\varkappa_p$ of this subgroup of compounds can be described satisfactorily by the relation [12]:

V. I. Lenin Khar'kov Polytechnic Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 2, pp. 212-216, February, 1978. Original article submitted December 6, 1976.

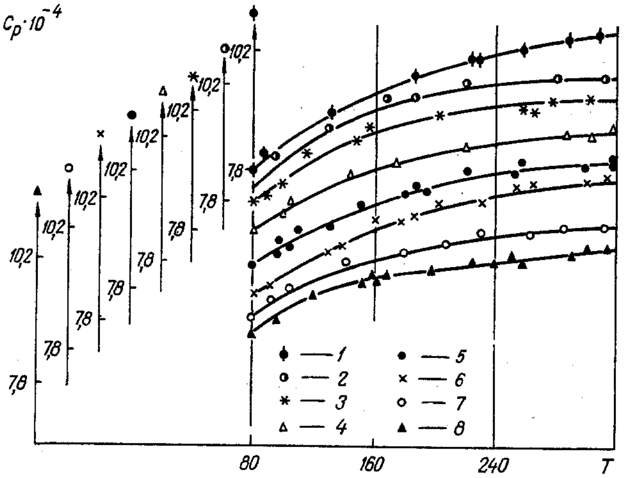

Fig. 1. Temperature dependence of the molar specific heat: 1) $LiSbS_2$; 2) $NaSbS_2$; 3) $KSbS_2$; 4) $RbSbS_2$; 5) $LiSbSe_2$; 6) $NaSbSe_2$; 7) $KSbSe_2$; 8) $CsSbS_2$; $C_p \cdot 10^{-4}$; J/kmole · K; T, K.

$$\varkappa_p = 10^3 C' \left(\frac{T_f\, \rho}{M}\right)^{1/2} \frac{T_f}{N^{1/2} T}, \qquad (2)$$

where C' is a coefficient chosen experimentally as a function of specimen structure.

The second group contains the compounds $NaSbSe_2$ and $KSbSe_2$. For $T > \Theta$ in the above temperature range the thermal conductivity decreases slightly with increase in temperature (Fig. 2b), which is due to the considerable structural defect. As was shown in [2], these compounds crystallize with NaCl structure (the three dimensional $O_h^5 - F_m3_m$ group) and have selenium at the nodes of the anion sublattice, with atoms of the alkali element and sulphur alternating statistically in the cation sublattice. The complexity of the cation sublattice causes strong distortions in the crystal potential field [13], and local density nonuniformity, due to a considerable difference in the atomic masses of sodium and sulphur. These two factors dictate a sharp increase in the anharmonic nature of oscillations of the crystal lattice, which mask variations in the anharmonic nature of oscillations due to temperature increase.

The third group contains the compounds $LiSbS_2$ and $LiSbSe_2$, whose thermal conductivity in the temperature range 80-350°K, as is shown in Fig. 2c is independent of temperature, due to the difference in the masses of lithium and sulphur. We note that the absolute value of the specific thermal conductivity of these compounds is almost an order of magnitude less than for the substances in the first and second subgroups. The low thermal conductivity and its independence of temperature for the lithium compound is due to the appreciable change in the heat-transfer mechanism. The structural disorder in these compounds is so great that the phonon mean free path, as estimated from the results of measurements of specific heat, speed of sound and thermal conductivity, is equal to $5.74 \cdot 10^{-10}$ m; i.e., it is less than the lattice parameter ($a = 5.74 \cdot 10^{-10}$ m).

In cases like these, as was first shown by Ioffe [14], each atom oscillates almost independently of the others, and the heat is transmitted by direct exchange of energy quanta between adjoining atoms. Because of the marked mass difference between lithium and sulphur this process of heat transfer in these compounds is very far from the resonance point at which the thermal conductivity [15] should increase with increase of temperature, and therefore there is no apparent temperature dependence of thermal conductivity, and its absolute value is very small.

Table 1 shows basic thermophysical parameters of the two groups of compounds of type $A^1SbC_2^6$. Analysis of the data shows that there are systematic variations in the properties of these compounds with increase of atomic number of the alkali elements and during transitions from sulphides to selenides.

An increase in atomic number of the alkali element in these compounds (apart from the lithium compounds) is accompanied by a decrease in thermal conductivity, due to growth of the average atomic mass of a compound and the appearance of a tendency for the crystalline structure to become complex and for it to break up during the Na → K → Rb → Cs.

TABLE 1. Basic Thermophysical Characteristics of the Compounds

Compound	Melting temperature, °K [1, 2, 8]	Density $\rho \cdot 10^{-3}$ $kg \cdot m^{-3}$ [1, 2, 8]	Ion value i, % [17]	Average atomic mass $\bar{A}$	Debye temperature Θ, °K	$\varkappa_p$, $W \cdot m^{-1} \cdot deg^{-1}$ at T=		$\vartheta \cdot 10^3$, $m \cdot sec^{-1}$ at 300°K
						Θ	300°K	
$LiSbS_2$	943	3,75	24,0	192	228	0,80	0,80	2,7
$NaSbS_2$	1011	3,58	27,5	208	218	3,40	2,22	2,7
$KSbS_2$	783	3,21	28,0	224	168	3,50	1,93	2,6
$RbSbS_2$	733	3,70	28,0	273	151	3,50	1,60	2,7
$CsSbS_2$	673	3,80	30,0	338	127		1,20	2,7
$LiSbSe_2$	993	4,94	20,2	276	185	0,60	0,60	3,1
$NaSbSe_2$	1013	4,68	21,5	292	174	1,48	1,40	3,1
$KSbSe_2$	733	4,33	25,0	308	142	1,36	1,30	3,1

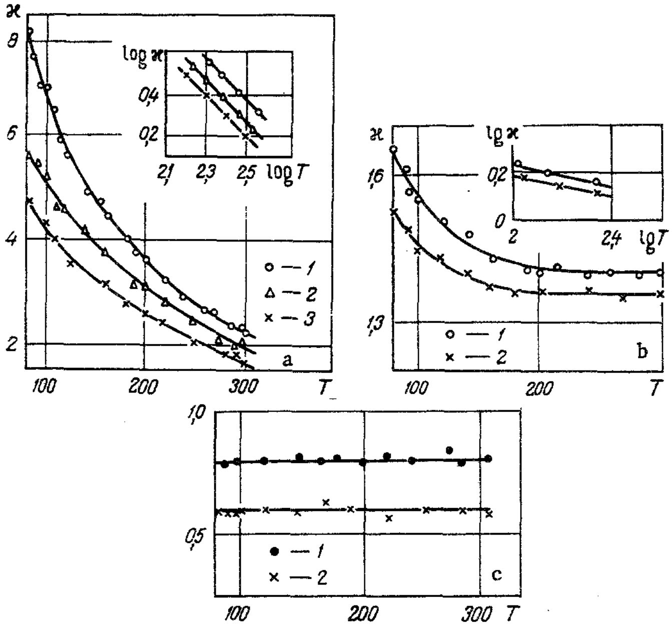

Fig. 2. Temperature dependence of the thermal conductivity: a) 1) $NaSbS_2$, 2) $KSbS_2$, 3) $RbSbS_2$; b) 1) $NaSbSe_2$, 2) $KSbSe_2$; c) 1) $LiSbS_2$; 2) $LiSbSe_2$. $\varkappa$, kW/m·K.

The transition from sulphides to selenides is also accompanied by a considerable decrease in thermal conductivity, and this is seen especially clearly when one compares the lattice thermal conductivities of these two groups of compounds at their respective Debye temperatures, when the thermal motion is developed in them to the same extent.

By investigating the systematic variation in thermal conductivity of binary compounds, Ioffe showed [16] that, due to an increase in the anharmonic nature of oscillations, the lattice thermal conductivity in these compounds decreases with increase of average atomic mass and during transition from covalent compounds to ionic compounds. A similar relationship also holds for compounds of type $A^1SbC_2^6$. These are characterized by a mixed ion-covalent bond with some fraction of the metallic components of the chemical bonds. The values presented in the table, from the data of [17], for the ion component of the chemical bond were calculated for isolated molecules. However, taking into account that there is an increase in the ion component of the chemical bond during transition from the molecular to the crystalline state, the data presented indicate that it increases in the direction Na → K → Rb → Cs and decreases in the direction S → Se.

In spite of the fact that in the transition $A^1SbS_2 \rightarrow A^1SbSe_2$ the ion component of the chemical bond decreases by 4-6%, the lattice thermal conductivity decreases. This apparent contradiction vanishes if one considers that there is an increase in the average atomic mass of the compounds by 40-50% in the transition S → Se, and this has a definite influence on the nature of the variation of the specific thermal conductivity.

The results of this experimental investigation of the systematic variations of thermal conductivity in compounds of type $A^1SbC_2^6$ are in good agreement with the anomalous increase in the width of the forbidden zone of these compounds during an increase in atomic number of the alkali element, occurring during a simultaneous drop in the fusion temperature and the microsolidity [2, 18].

However, analysis of the experimental data shows that the influence of the degree of the ionic nature of the chemical bond and the increase in the average atomic mass on the thermal conductivity of $A^1SbC_2^6$ compounds and its temperature dependence do not appear in simple form. Apparently, one must also take into account the structural features of the compounds, as well as the electronic configuration of the constituent atoms.

NOTATION

Θ	is the Debye temperature;
T_f	is the fusion temperature;
$\bar{A}$	is the average atomic mass of the compound;
ρ	is the density of the substance, kg/m^3;
C	is a constant;
M	is the molecular mass of the compound;
N	is the concentration of atoms;
T	is the temperature;
$\varkappa_p$	is the lattice thermal conductivity;
a	is the lattice parameter;
ϑ	is the speed of sound propagation, $m \cdot sec^{-1}$.

LITERATURE CITED

1. S. I. Berul, V. B. Lazarev, and A. V. Salov, Zh. Neorg. Khim., 16, 3363 (1971).
2. V. A. Bazakutsa, N. I. Gnidash, V. B. Lazarev, E. I. Rogacheva, A. V. Salov, L. N. Sukhorukova, M. P. Vasil'eva, and S. I. Berul, Zh. Neorg. Khim., 18, 3234 (1973).
3. V. M. Mogilevskii and A. F. Chudnovskii, Thermal Conductivity of Semiconductors [in Russian], Nauka, Moscow (1972).
4. E. A. Petrov and E. L. Strum, Fiz. Tverd. Tela, 4, 6 (1962).
5. D. P. Spitzer, J. Phys. Chem. Solids, 31, No. 1, 19 (1970).
6. V. A. Bazakutsa, N. In. Gnidash, E. I. Rogacheva, A. V. Salov, S. I. Beruland, and V. B. Lazarev, Izd. Akad. Nauk SSSR, Neorg. Mater., 9, 1890 (1973).
7. V. A. Bazakutsa, N. I. Gnidash, V. B. Lazarev, E. I. Rogacheva, A. V. Salov, S. I. Berul, and M. P. Vasil'eva, Zh. Neorg. Khim., 19, 488 (1974).
8. Yu. A. Buslaev, E. A. Kravchenko, I. V. Kuz'min, V. B. Lazarev, and A. V. Salov, Zh. Neorg. Khim., 16, 3367 (1971).
9. F. I. Ostrovskii, R. P. Krentsis, and P. V. Gel'd, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 9, 112 (1969).
10. E. D. Devyatkova and V. V. Tikhonov, Fiz. Tverd. Tela, 9, 773 (1967).
11. J. R. Drabble and E. J. Goldschmid, Thermal Conduction in Semiconductors, Pergamon (1961).
12. A. Misnar, Thermal Conductivity of Solids, Liquids, Gases and Their Compounds [Russian translation], Mir, Moscow (1968).
13. Z. S. Medvedeva, Chalcogenides of Elements of Subgroup IIIB of the Periodic System [in Russian], Nauka, Moscow (1968).
14. A. F. Ioffe, Fiz. Tverd. Tela, 1, 160 (1959).
15. A. S. Okhotin, A. S. Pushkarskii, and V. V. Gorbachev, Thermophysical Properties of SemiConductors [in Russian], Atomizdat, Moscow (1972).
16. A. F. Ioffe, Fiz. Tverd. Tela, 5, 3336 (1963).
17. M. I. Golovei, E. E. Semrad, E. Yu. Peresh, and Yu. V. Voroshilov, in: Some Aspects of the Chemistry and Physics of Semiconductors of Complex Composition [in Russian], Uzhgorod (1970), p. 145.
18. V. A. Bazakutsa, in: Proceedings of the International Conference on Amorphous Semiconductors-74, Reinkhardsbruni (1974), 186.