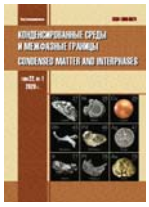

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Study of the thermal conductivity of PbS, $CuFeS_2$, ZnS

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Abstract

It is necessary to know the values of the thermal conductivity coefficient of a semiconductor material to assess the possibility of its application as a thermoelectric. The thermal conductivity of natural minerals of galena (PbS), chalcopyrite ($CuFeS_2$), and ZnS ceramics was studied using the absolute stationary method of longitudinal heat flux in the range of 50–300 K.
The samples were homogeneous, had low impurity content (the chemical composition of the samples was controlled by the X-ray fluorescence method) and were characterized by high electrical resistivity ($\rho > 9 \cdot 10^{-2}$ Ohm·m at room temperature). It corresponds to the electronic component of the thermal conductivity $k_e < 1 \cdot 10^{-4}$ W/(m·K). The results of the thermal conductivity measurements are presented graphically and in tabular form. All the dependences are shown to be decreasing. The thermal conductivity values (W/(m·K)) at 50 K amount to 10.9 for PbS, 62 for $CuFeS_2$, and 73-98 for ZnS. At 300 K the values are 2.48, 10.5 and 18.6 – 18.8 W/(m·K), respectively.
All the studied materials have much worse thermal conductivity than pyrite (FeS_2). The obtained data was compared to the data available in literary sources. The temperature dependence of the thermal conductivity of galena is low, its low thermal conductivity is favourable for thermoelectric applications.
The thermal conductivity of chalcopyrite, which was detected in this study, appeared to be the highest among the corresponding literature data. The high thermal conductivity of zinc sulphide correlates to its wide variability depending on the structural features of the material. The temperature dependences of the mean free path of phonons were calculated. The values of this characteristic, estimated for the melting temperature, for PbS and for ZnS, in particular, significantly exceed the size of an elementary crystal cell, which is unusual.

Keywords: mineral, galena, chalcopyrite, ceramics, zinc sulphide, thermal conductivity, temperature dependence.

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1. Introduction

Sulphides are a vast class of compounds with a semiconductor nature of electrical conductivity [1]. It is necessary to know the values of the thermal conductivity coefficient to determine the scope of application of a solid material, including its application as a thermoelectric [2]. The feature of this characteristic is its considerable variability depending on temperature, impurity composition, and structural features of the material. The existing theoretical concepts of heat transfer processes do not allow reliable and accurate a priori estimates of thermal conductivity, and the experimental method is the only reliable way to determine it.

So far, a number of experimental studies researching the thermal conductivity of pyrite (FeS_2) [3], galena (PbS) [4–9], chalcopyrite ($CuFeS_2$) [10–14], and zinc sulphide [15–19] are known. The results obtained in these studies vary greatly in the absolute value of thermal conductivity as well as in the nature of its temperature dependence.

The aim of this study was to conduct an independent research of temperature dependence of the thermal conductivity of the natural minerals of galena and chalcopyrite (Ural region), and also of synthetic zinc sulphide ceramics.

2. Experimental

Thermal conductivity in the range of 50–300 K was measured using the absolute stationary method of longitudinal heat flux. The experimental equipment and methods are described in [20]. PbS and $CuFeS_2$ samples were about 9×9×24 mm in size, see Fig. 1, 2, ZnS – 5×5×40 mm. The measurement error for the value of thermal conductivity was no more than ± 5 %.

The chemical composition of the samples was controlled using the X-ray fluorescence method on "SUR-01 Renom". The X-ray tube had copper anode, its voltage was 30 kV, and its current amounted to 4800 μA. A vanadium filter (100 μm) was used.

X-ray phase analysis was performed using the DRON-7 diffractometer with cobalt anode of the tube (λ_m = 1.79021 Å).

The PbS sample was cut from a homogeneous, monolithic piece of galena (see the photo on Fig. 1) with a mass of about 0.5 kg. The study of its chemical composition did not reveal any impurities with an accuracy of 0.01 wt. % with respect to Pb. In this regard, the resistivity measured at room temperature turned out to be $\rho = 9 \cdot 10^{-2}$ Ohm·m. This is a sufficiently high value that, using the Wiedemann-Franz-Lorentz law, the electronic component of thermal conductivity $k_e < 1 \cdot 10^{-4}$ W/(m·K) can be considered negligible compared to the experimentally determined.

The $CuFeS_2$ sample (see the photo on Fig. 2) was cut from a homogeneous, monolithic piece of chalcopyrite. The X-ray powder diffraction pattern of this sample is given in Fig. 3. It is almost identical to the diffraction patterns obtained in [13].

The results of the chalcopyrite sample chemical composition study are given in Table 1. The probes were taken from different parts of the sample.

Fig. 1. Photo of a galena monolith with a piece cut off for a sample

Fig. 2. Photo of a chalcopyrite monolith with a piece cut off for a sample

Table 1. Content (wt%) of chemical elements in the chalcopyrite sample

Element	Probe number			
	1	2	3	4
Fe	35.03	40.29	39.97	38.09
Cu	60.61	59.48	59.71	60.98
Zn	0.00	0.00	0.00	0.359
Ar	0.213	0.107	0.325	0.338
Mn	0.151	0.117	0.00	0.280

We can see little deviation in the chemical composition in terms of homogeneity and the low impurity content. The resistivity and electronic component of the thermal conductivity at room temperature were close to those determined for galena.

One of the zinc sulphide samples (OOO PromLab, Nizhniy Novgorod, Russia) was obtained using the method of chemical deposition from the gas phase by the reaction between zinc vapour and hydrogen sulphide. The sample carved for the thermal conductivity measurement was 5×5×40 mm in size, its major axis was perpendicular to the growth direction of the material. Zinc sulphide of the FLIR grade is a highly purified material (its chemical purity of metal impurities is 6N), its electrical conductivity is, consequently, very low. The average grain size is about 10 μm, the density is more that 99.99 % of the theoretical value. The material is suitable for optical applications in IR equipment and its transparency is in the range of 1–13 μm. In the visible range, ZnS scatters radiation due to the presence of an insignificant share of the hexagonal wurtzite phase alongside with the cubic sphalerite phase.

The second sample of zinc sulphide was submitted by A.G. Soldatov. (Minsk, Belarus, Scientific Production Centre of Material Studies) After fabrication for the measurement, it had dimensions of 8×6×20 mm. Its electrical conductivity was negligibly low.

3. Results and discussion

In Fig. 4 there is a temperature dependence graph of the thermal conductivity $k(T)$ of the galena sample. For comparison, the results obtained by the authors of other studies are also given (the coordinates of the $k(T)$ points were obtained by the method of digitization of the shown graphs).

It can be seen that in the region of nitrogen temperatures our $k(T)$ values are close to those obtained for one of the few synthesized single crystals in [9]. However, they are significantly lower than those given in [4]. Low-temperature thermal conductivity is known [21] to be particularly sensitive to various structural features of the material. It should be noted that extrapolation of our data to the $T > 600$ K area (dotted line in

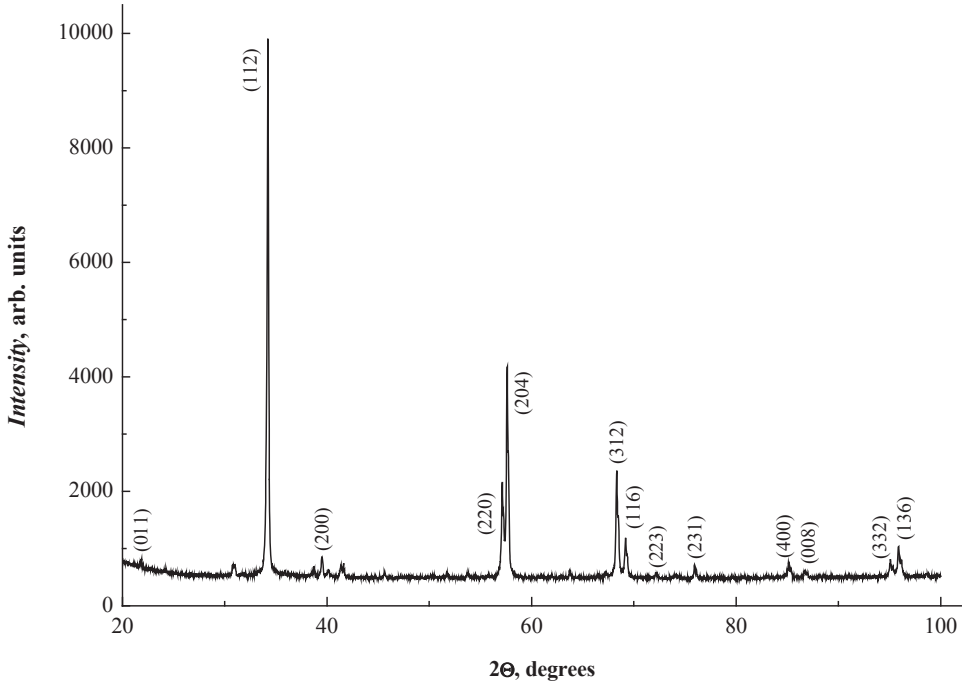

Fig. 3. Powder diffraction pattern of the chalcopyrite sample

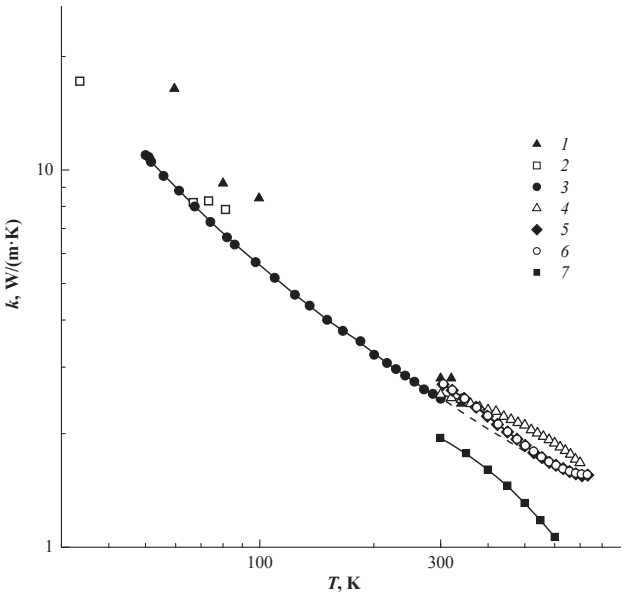

Fig. 4. Temperature dependence of the thermal conductivity of galena: (*1*) [4], (*2*) [9], our data (*3*), (*4*) [8], (*5*) [6], (*6*) [5], (*7*) [7]

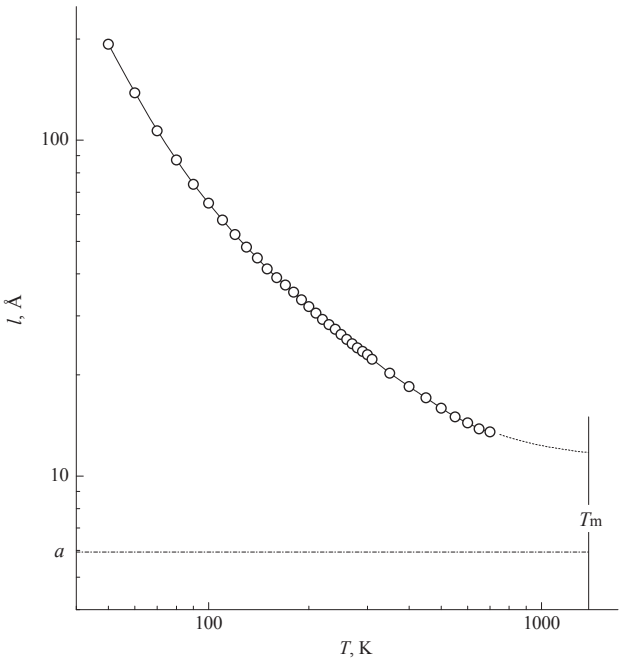

Fig. 5. Temperature dependence of the mean free path of phonons in PbS

Fig. 4) almost matches the data in [5, 6]. This allows us to evaluate the latter as common to the PbS crystalline matrix.

The $k(T)$ curve, obtained in [7], turns down. And in the sector of the highest temperatures when describing the behaviour of thermal conductivity by $k(T) \sim T^n$ function, the parameter value is $n > 1.1$, which seems doubtful, especially taking into consideration the very low values of thermal conductivity. In the aforementioned study the thermal conductivity was determined from the temperature conductivity using the temperature dependence of the heat capacity, calculated by Debye's theory. However, it is well known that actual behaviour of thermal conductivity of many compounds differs significantly from that of Debye's theory. Indeed, as shown in [22, 4], the PbS thermal conductivity increases sharply when the temperature reaches room values and continues to increase until the melting point [23].

The authors [8] used their own heat capacity data to define the behaviour of thermal conductivity, which, in our opinion, are in doubt. We associate the $k(T)$ downward curve, obtained in this study, with this circumstance.

In Fig. 5 there is a graph of temperature conductivity of the mean free path of phonons $l(T)$ in galena. It was determined from Debye's expression

$$k = C \cdot v \cdot l/3, \quad (1)$$

where C is the thermal conductivity of a volume unit, v is the mean free path of phonons (sound). The phonon thermal conductivity model can be provisionally used not only for monocrystals but also for significantly disordered media. We used our data regarding thermal conductivity, their extrapolation to the area of high temperatures, thermal conductivity data from [4] and [23] for our calculations. The value $v = 2040$ m/s from [5] was taken as the average speed of sound.

It can be observed that the temperature dependence $l(T)$ is relatively low. In the 50–300 K temperature range the l value changes by only one order of magnitude. Such behaviour of $l(T)$ indicates a significant manifestation of phonon scattering, which is characteristic for the polycrystalline compound of the material. In the range of melting temperature, the value l, obtained by extrapolation, is 2 times higher than the parameter of the PbS crystal cell. Note that for many monocrystals with different matrix chemical compositions and structures, the minimum value of l, determined similarly, is close to the cell parameter or comparable to the average interstitial distance in the crystal [24, 25]. It seems to be difficult to explain the obtained large value of l_{min} for galena. As follows from the

equation (1), the restrictions on the choice of heat capacity components effective for heat transfer can only lead to an increase in the calculated values of *l*. Bipolar contribution to the measured PbS conductivity noted in [5,6] in the context of our sample with small impurity content should be negligibly low.

The results of the thermal conductivity measurements of chalcopyrite are presented in Fig. 6. For comparison there are also given the data of other authors (the coordinates of the $k(T)$ points were obtained by the digitization of the graphs in the figures).

It can be seen that the current data regarding the thermal conductivity of chalcopyrite varies significantly. The thermal conductivity of the natural sample examined at temperatures below room temperature is significantly higher (Fig. 6, curve *1*) than that of the synthesized samples. Taking into account the small impurity content it clearly indicates a lesser degree of disorder in the structure. The temperature behaviour of our graph $k(T)$ is close to that defined in [12] (curve *4*).

Slowing down of the $k(T)$ dependency decrease, revealed in [11] (curve *2*) is, apparently, due to the non-lattice contribution to the thermal conductivity. In study [13] the chalcopyrite sample synthesized by melting-annealing-sintering process was studied, which had Fe/Cu atomic ratio of 1.005. We used the heat capacity (Const(T) defined using Dulong–Petit law to calculate the thermal conductivity from the measured temperature conductivity. In fact, the heat capacity of chalcopyrite increases with temperature. According to the data in [26] it is close to the limit value of $3R \times 4 = 100$ (J/(mol·K) already at room temperature, which is far from melting temperature, and it continues to increase. These data were in good agreement with the high temperature results obtained in [27]. This is probably why the $k(T)$ graph of the authors [13] (curve *6*) in our Fig. 6 with the selected scale has an unusual shape, in that it bends sharply downwards. In the range of room temperature, the exponent n in the expression $k(T) \sim T^{-n}$ is more than one and for the highest temperatures $n > 2$.

The results of the thermal conductivity measurement of the sample of $Cu_{25.43}Fe_{25.66}S_{48.91}$ [14] (curve *5*) are the closest to the data in [13]. In that study the authors took into account the experimentally determined temperature dependence of heat capacity. However, no numerical heat capacity data are given in that article.

A possible explanation for the great decrease in high temperature heat conductivity reported in [13, 14] may be the proximity to the Neel temperature $T_N = 823$ K [28, 29].

The authors of study [10] examined a polycrystal that did not undergo a complete annealing procedure after synthesis. The glass-like nature of the temperature dependence of its thermal conductivity (curve *3*)) is associated with the inhomogeneity of the sample. But the positioning of the two $k(T)$ points close to room temperature raises questions about possible changes in the experimental method or the quality of the sample, and also about the shape of a part of the graph which can be extrapolated to the sector of elevated temperatures.

In Fig. 7 there is a graph of temperature dependence of the mean free path of phonons in the studied chalcopyrite sample in accordance with expression (1). The calorimetric data from [26, 27] were taken into account. The value

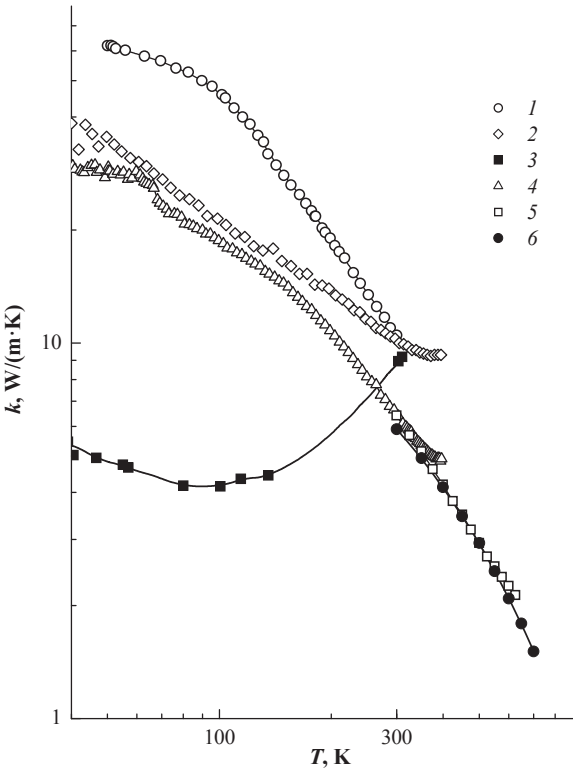

Fig. 6. Temperature dependence of the thermal conductivity of chalcopyrite: (*1*) our data, (*2*) [11], (*3*) [10], (*4*) [12], (*5*) [14], and (*6*) [13]

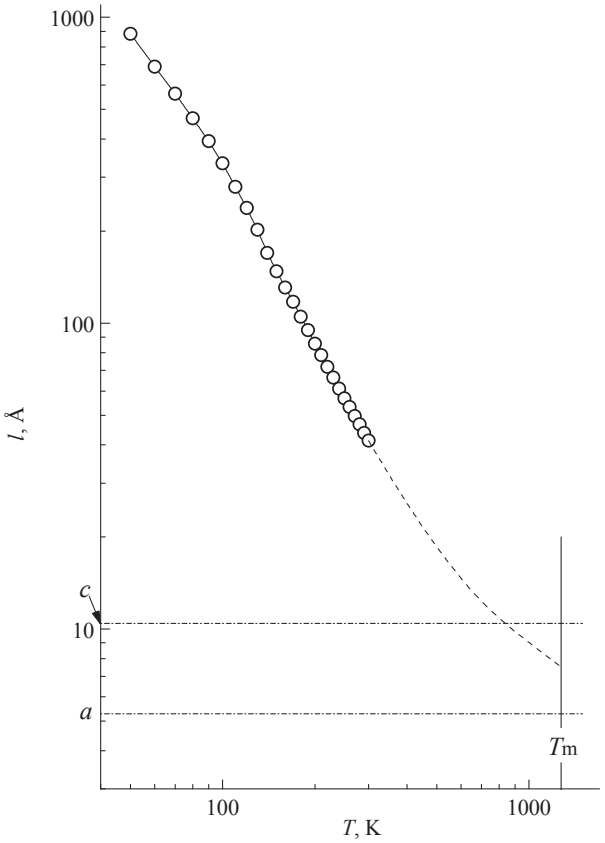

Fig. 7. Temperature dependence of the mean free path of phonons in chalcopyrite

v = 2040 m/s determined in [13] was taken as the average speed of phonons.

A slowdown of the growth of $l(T)$ in condition of the decrease in temperature from T = 100 K demonstrates the manifestation of phonon-defect scattering. In the range of room temperature, the $l(T)$ value decreases rapidly, namely in proportion to $T^{-1.6}$. Extrapolation of the graph to the melting temperate range of $CuFeS_2$ gives us the l_{min} value, which is an intermediate between the values of a and c parameters of the crystalline lattice of this compound.

The results of the thermal conductivity measurements of two ZnS samples are presented in Fig. 8. The zinc sulphide thermal conductivity data of other authors were also presented there (the numerical data of [16,17] were used, in other cases the coordinates of the $k(T)$ points were obtained by digitization of the curves presented in the figures in the articles).

Significant differences in the given graphs indicate strong sensitivity of the ZnS thermal conductivity to the impurity composition and

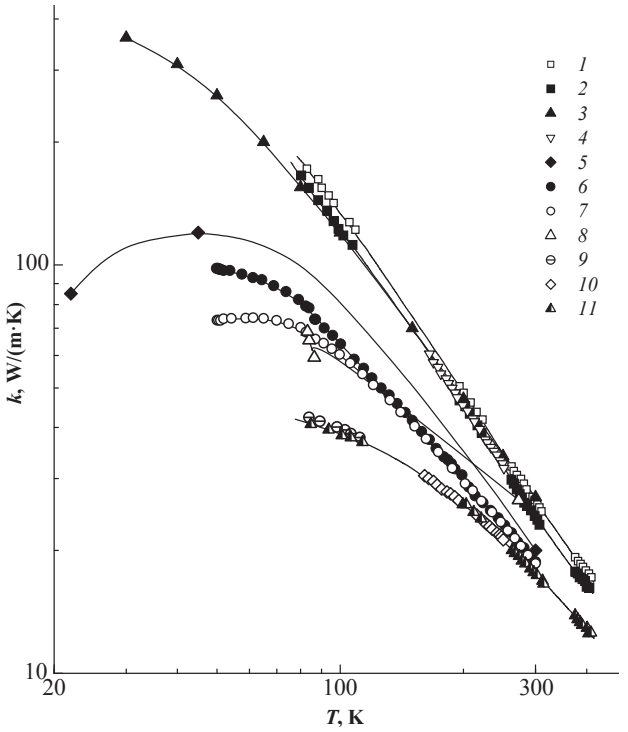

Fig. 8. Temperature dependence of the thermal conductivity of ZnS: (*1*), (*2*), (*4*), (*9*), (*10*), (*11*) [18], (*3*) [15], (*5*) [17], (*6*) and (*7*) our data, and (*8*) [16]

structural features of the material. The $k(T)$ curves of monocrystalline ZnS samples studied in [15,18] are given above the other ones. Based on a slightly higher thermal conductivity in the sector of the lowest studied temperatures, it can be argued that the Luguevs [18] sample (Fig. 8, curve *1*) had the most perfect structure. Moreover, the polycrystalline ZnS sample [18] also demonstrates (curve *2*) a higher thermal conductivity at low temperatures than Slack's monocrystal [15] (curve *3*). In this regard, we note that phonon scattering at the boundaries of crystalline grains with cubic symmetry may be insignificant even at sub nitrogen temperatures [30]. In study [16] the object of the research was the natural mineral of sphalerite, which can explain the features of the obtained $k(T)$ dependence.

As for our samples, their $k(T)$ curves are located between the graphs for a monocrystal studied by Krueger [17] (curve *5*) and porous polycrystals from [18] (curves *9*, *10*, *11*). The $k(T)$ graphs that we obtained have indications of their reaching the low temperature maximum. It is known that with an increase in the structure defectiveness, this

maximum decreases and usually shifts toward higher temperatures [21].

The lesser low temperature thermal conductivity of the sample by OOO PromLab (curve *7*), taking into consideration its chemical purity, can be explained by phonon scattering due to the presence of the hexagonal wurtzite phase in it.

In Fig. 9 there is a graph of temperature conductivity of the mean free path of phonons $l(T)$ in this sample. The calorimetric data from [31] were taken into account, the value of v = 2.86 km/s calculated using the elastic modules from [32] was taken as the average speed of sound.

It can be observed that in the temperature range of 100–300 K the obtained dependence is satisfactory described by the power function $T^{-1.61}$. Moreover, in the room temperature range, the value of l remains significant (~ 102 Å). Note that it is 2 times smaller than the l value determined in [18] by another method, provided that the difference in thermal conductivity is only ~ 1.5 times. Extrapolating our $l(T)$ graph to the ZnS melting temperature range gives us the value of l_{min} which is almost 4 times higher than the lattice parameter a. This circumstance seems to indicate the features of the phonon-phonon interaction in this compound.

The data presented in Table 2 demonstrate a contrasting difference in the values of the thermal conductivity coefficient of the studied compounds. We should note the high value of the thermal conductivity of chalcopyrite, which indicates the ordered arrangement of cations in the lattice. The very low thermal conductivity of galena attracts attention, being unusual for compounds with a simple lattice (such as sodium chloride). This property means it is favourable for the development of thermoelectric materials. The high thermal conductivity of zinc sulphide favours its use in photonics.

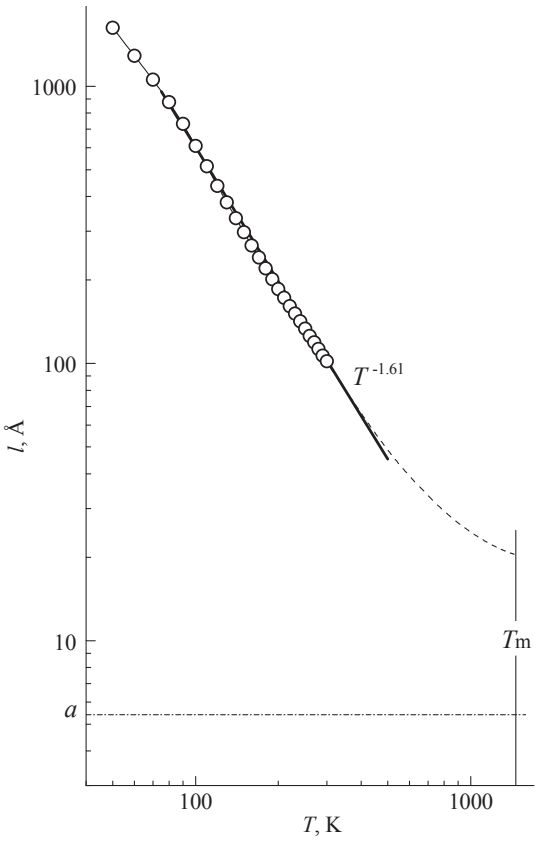

Fig. 9. Temperature dependence of the mean free path of phonons in the ZnS sample

4. Conclusion

Thus, experimental data were obtained that substantially complement the concepts of the thermal conductivity of the natural minerals of chalcopyrite and galena, as well as synthetic ceramics of zinc sulphide. These data indicate the fundamental prospects of natural sources of raw materials for instrument engineering. The low thermal conductivity of galena means its use is favourable for thermoelectric applications. On the other hand, the wide variability of the thermal conductivity coefficient of these compounds depending on the state of the material was revealed. In the future, it is planned to expand the

Table 2. Thermal conductivity values of the studied sulphides at different temperatures

T, K	PbS	$CuFeS_2$	ZnS PromLab	ZnS (Minsk)	FeS_2 [3]
50	10.9	62	73.2	98	900
100	5.6	46.5	60.0	64	207
150	4.02	27.8	40.9	41.6	106
200	3.27	18.8	29.5	30.0	73
250	2.79	13.6	23.1	23.3	58
300	2.48	10.5	18.6	18.8	48

research into the thermal conductivity of natural sulphide minerals from various deposits.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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