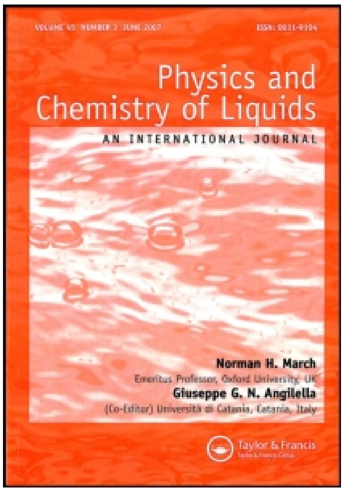

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Experimental Investigation of Heat Conductivity of PbTe and PbSe in Solid and Liquid States

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Abstract—There has been measured heat conductivity of PbTe up to 1350° and PbSe up to 1500 °K. The investigations were carried out by using the flat layer method and the coaxial cylinders method. The relative error of the measurements did not exceed 10%. The contribution of separate components into the total heat conductivity was determined by calculation. There has been found a considerable deviation from the Wiedemann-Franz law in case L_{exp} of PbTe melt equals approximately 0.5 L_0 (Sommerfeld Lorentz number).

The heat conductivity of lead chalcogenides was studied sufficiently widely almost within the whole temperature range(1–9) except for the range preceding the melting and liquid state. It is shown(1,2) that, irrespective of the concentration of the carriers, within the temperature range from 90 °K to 440 °K the heat resistance of the PbSe lattice conforms to Eiken's law. As a result of the investigations of heat conductivity of PbTe and PbSe, carried out at higher temperatures up to 800 °K,(3) there has been found at $T > 300$ °K an additional component (in addition to the phonon and electron ones) in the heat conductivity of these compounds. This additional mechanism keeps within the framework of the bipolar thermal diffusion of the carriers, taking into account the temperature dependence of the width of the forbidden band. And, finally, a more detailed consideration of the additional components of the PbTe and PbSe heat transfer in these substances has shown(4) that within the temperature range from 500 °K to 700 °K, along with the bipolar thermal diffusion, a small contribution (5% from the total heat conductivity) is made by the phonon mechanism. Of particular interest are the papers$^{(6,7)}$ which aimed to experimentally divide the two basic components of the heat conductivity, i.e. the electron and phonon ones. It has turned out that for PbTe and PbSe the value of Lorentz experimental number constitutes $\sim 0.4 \div 0.6\, L_0$, wherein L_0 is its theoretical value for this particular degree of degeneracy. It is natural that these results were obtained at sufficiently low temperatures of an order of 100 °K which allow to carry out numerous limiting conditions of the experiment. The authors of Refs. 8 and 9 attribute the observed deviation from Wiedemann-Franz law to a possible increase in the heat resistance due to non-elastic interelectronic collisions taking place within the framework of the mechanism proposed by Zeimann.$^{(10)}$ Even this incomplete enumeration of papers makes it possible to agree with the opinion that the heat conductivity of lead chalcogenides has been studied rather thoroughly, and its mechanism up to high temperatures should be considered established.

In the present paper the heat conductivity of PbTe and PbSe was studied in the temperature range of from 300 °K to the premelting region and in the melt. With this purpose in view, there were synthesized polycrystalline samples of PbTe and PbSe with Hall's concentration of the carriers at room temperature $P = 2.10^{18}\,\mathrm{cm}^{-3}$ and $n = 8.10^{17}\,\mathrm{cm}^{-3}$, respectively. In the solid state the heat conductivity was measured by the flat layer method,$^{(11)}$ and in the range preceding melting and in the melt—by the radial heat flux method.$^{(12)}$ The maximum relative error of the measurements did not exceed ±10%.

Figures 1 and 2 show temperature dependence obtained by us, and calculated separate components of the mechanism of the heat transfer of said compounds. Shown here are only high-temperature parts of the dependences, as investigations carried out at lower temperatures give nothing that would be absolutely new. At temperatures somewhat exceeding room temperature the heat conductivity of lead selenide varies in accordance with the T^{-1} law, which is in agreement with the principal part played by the phonon heat transfer at these temperatures. There was made a calculation

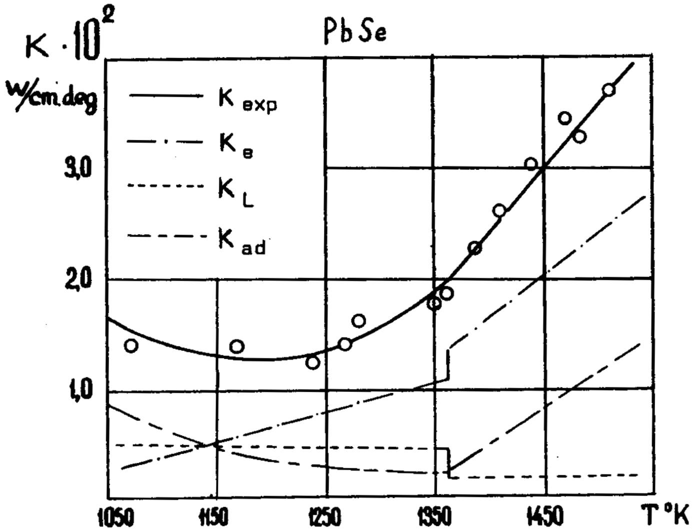

Figure 1. Temperature dependence of heat conductivity and its components for plumbum selenide: κ_{exp}—experimental values of heat conductivity, κ_e—electron heat conductivity, κ_L—photon heat conductivity, κ_{ad}—additional heat conductivity.

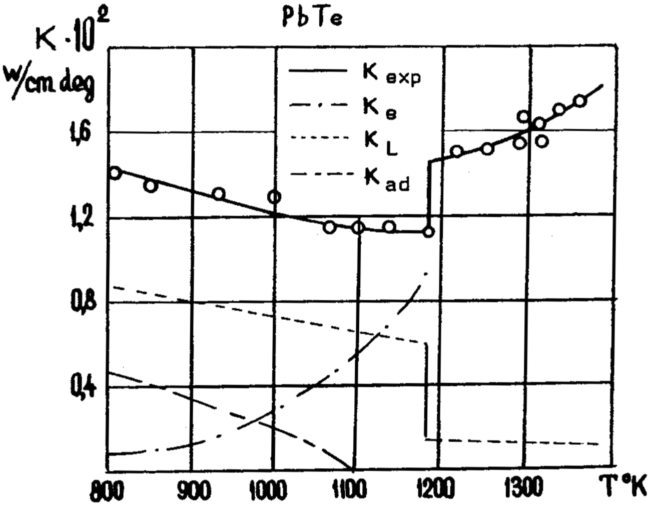

Figure 2. Temperature dependence of heat conductivity and its component for plumbum telluride.

of the constant in the dependence on $\kappa_L = \text{const} \cdot T^{-1}$ whose value turned to be equal to 5.6 w/cm. However, already at 400 °K there is observed a deviation from the law. We attribute this deviation to the diffusion of the electron-hole pairs since the electric conductivity of lead selenide acquires its own character. The bipolar heat conductivity was calculated in accordance with Davydov–Shmushkevitch equation by assuming that the mechanism of diffusion had the greatest effect on the atomic oscillations of the lattice:

$$\kappa_{\text{ad}} = \left(\frac{k}{e}\right)^2 \frac{\sigma_n \cdot \sigma_p}{(\sigma_n + \sigma_p)^2} \left(4 + \frac{\Delta E}{kT}\right)^2 \sigma T, \tag{1}$$

wherein: E is width of the forbidden band; σ_n; σ_p are partial contributions of electrons and holes into kinetic effects.

The partial contribution of the electrons and holes into the electric conductivity was evaluated on the basis of the ratio of mobilities, which according to Ref. 13 at room temperature equals approximately 1.4. The approximation of such an evaluation is evident, and this, apparently, results in the fact that at $T = 800$ °K the additional heat conductivity is much inferior by its value to the calculated bipolar thermal diffusion, as at $T = 1{,}000$ °K $\kappa_{\text{ad}} = 2.3 \cdot 10^{-2}$ w/cm.deg, whereas $\kappa_{\text{ad}} = 0.3 \cdot 10^{-2}$ w/cm.deg. Thus, the coefficient $\sigma_n \cdot \sigma_p/\sigma^2$ in Eq. (1) is a variable value, the more so in view of the fact that in accordance with Ref. 14 the effective mass of the holes in lead selenide increases much more rapidly than that of the electrons. Therefore, in our opinion it is more expedient to calculate the coefficient $\sigma_n \cdot \sigma_p/\sigma^2$ on the basis of the experimental additional heat conductivity, and to use its value thus obtained for the evaluation of the ratio of the carrier mobilities. It has turned out that at 1,100 °K the mobility of the electrons is by an order greater than that of the holes. This result has proved rather interesting as it correlates with the results of Ref. 15 in which Hall effect taking place in lead chalcogenides at high temperatures was investigated. For instance, it was found for PbTe that at 800 °K $U_n/U_p = 9$. This difference can be explained by using a model having a complex structure of the valence band. Assuming that within this temperature range only heavy holes participate in the kinetic effects in PbSe, it becomes clear why the partial contribution made by the hole conductivity is small. As is seen from Fig. 1, the melting of lead selenide is not accompanied by any jump changes in the total heat conductivity, though this cannot be said with respect to its separate components. The electron component, as calculated by the conventional method in accordance with Wiedemann-Franz law, increases from $1 \cdot 10^{-2}$ w/cm.deg to $1.4 \cdot 10^{-2}$ w/cm.deg (in the temperature range of from 1,000 to 1,500 °K). The data relating to the electric conductivity and thermal electro-motive force, that were necessary for the present calculation, were taken from Ref. 16. On the other hand, the evaluation of the molecular heat transfer in the melt, made in accordance with the equations of Bridgeman and Weber,(17) has shown that the lattice heat conductivity decreases down to $0.17 \cdot 10^{-2}$ w/cm.deg immediately after the melting and exhibits a weak tendency to drop as the temperature rises. When making calculations in accordance with these equations it was assumed that the heat capacity and group velocity of phonons do not vary in these substances in the course of melting. The values C_p and V_{gr} are in full accord with the results of Refs. 18 and 19. Thus, the different direction of the change of the two main components of PbSe heat conductivity in the course of melting provides for a smooth transition from the solid state into the liquid one. A further temperature development of the heat conductivity, however, shows that there exists an additional component of the heat transfer in addition to the calculated electron and molecular components. This apparently results from the fact that, when in the melt $(\partial\sigma_0/\partial T > 0;\ \partial\alpha/T < 0)$, lead selenide is a strongly pronounced inherent semiconductor, the absolute values of these characteristics being typical for inherent semiconductors. As a result of this, the additional heat transfer can be realized similarly to the bipolar heat conductivity in the crystalline phase. It is impossible, however, to calculate the contribution made by this component in the melt as there is no method of evaluating the partial contributions σ_n and σ_p into the total electric conductivity. At any rate, the solution of the reverse task has shown that at 1,500 °K $\sigma_n/\sigma_p \approx 18$. The substantial increase in the ratio, as compared to the premelting region, is mainly connected, in our opinion, with an increase in the concentration of the electrons during melting.

Figure 2 shows a temperature dependence of the heat conductivity of lead telluride in the premelting region and in the liquid state. As well as in the case with lead selenide, the results obtained at 300 °K well coincide with those obtained in Ref. 3. The analysis of the mechanism of the heat transfer in the solid phase was carried out in the conventional way. The phonon component of the heat conductivity was determined within the whole temperature range by observing the conditions providing for the action of the T^{-1} law. The product $\kappa_L \cdot T$ turned out to be equal to 7.1 w.cm. The electric conductivity of the samples decreases up to 500 °K, whereupon there is observed a range of intrinsic conductivity. At this temperature and higher the total heat conductivity starts exceeding $\kappa_L + \kappa_e$, and it is the bipolar diffusion that makes its contribution. The bipolar component is calculated in accordance with Davydov–Shmushkevitch equation, assuming, at the same time, that the ratio of mobilities $U_n/U_p \approx 2.5$.(20) This mechanism satisfactorily describes the additional heat conductivity up to $T \approx 800$ °K but further on exceeds considerably the experimental values of κ_{ad}. It is probable that this is also a result of the peculiarities of the structure of the energy bands. Whereas in the case of PbSe we could cite but a circumstantial evidence of the complex structure of the valence band, with respect to PbTe the abovementioned paper(15) and a number of other papers(21,22) have shown on the basis of high-temperature investigations that the valence band consists of two sub-bands, namely, those of light and heavy holes, and at the temperature of approximately 600° and higher all the kinetic effects are caused by the electrons and heavy holes. According to Ref. 15 the ratio between the mobility of the electrons and that of the holes turned out to be equal to nine at 800 °K. It is evident that the calculation of the bipolar diffusion with $U_n/U_p = 2.5$ within the whole temperature range is not correct, and the difference between the calculated values of the heat conductivity of the electron-hole pairs and the experimental additional heat conductivity is caused just by the temperature dependence of the ratio of the mobilities. In this connection of a particular interest is the evaluation of the partial contributions into the electric conductance of the electrons and holes. For this purpose we used Davydov–Shmushkevitch equation along with the assumption that the whole additional heat conductivity is caused by the bipolar diffusion of the carriers. It has turned out that at 800 °K $\sigma_n/\sigma_p = 7$, i.e. we have got a value close to the ratio of the mobilities. This is a rather useful result as, firstly, it corroborates absolutely independently the presence of a complex structure of the valence band of PbTe, and, secondly, opens up new posibilities for the high-temperature investigations used in order to study the energy spectrum of the carriers. A further increase in the temperature is accompanied by a decreased part played by the holes in the kinetic effects, for instance, in the heat conductivity, and at $T > 1{,}100\ ^\circ\mathrm{K}$ the contribution made by the bipolar diffusion into the total heat conductivity is extremely small (Fig. 2). In the course of melting the heat conductivity of PbTe jumps. It is evident that, in this case, the character of the change of the total heat conductivity determines the behaviour of the electron component. The molecular component calculated in accordance with the equations of Bridgeman and Weber is much inferior to it by its value (Fig. 2). An analysis of the electronic heat transfer, however, has demonstrated a rather interesting fact: the values calculated in accordance with Wiedemann-Franz law are much greater than the experimental data. It is suffice to say that Lorentz experimental number equals approximately $0.5\,L_0$ even if in the course of the calculations use was made of the values of the electric conductivity of the PbTe melt, which were taken from Ref. 23 and are by 50% smaller than the data.(16) Because of this, the heat conductivity of liquid lead telluride was measured particularly carefully; there were measured four cells with different gaps and use was made of two types of thermocouples, the results shown in Fig. 2 being reproduced in all the cases. It should be noted in this connection that this is not the only fact of negative deviation from Wiedemann-Franz law for the case of liquid metals and semiconductors metallizing during melting.(24,25)

What are the theoretical prerequisites of this anomaly? It seems that its cause should be looked for in possible non-elastic interactions taking place in the electron–phonon and electron–electron systems. A. I. Gubanov,(26) for example, when considering the changes of the function of the distribution of electrons under the action of atomic oscillations, arrives at the conclusion that in liquid the electrons may disperse on the phonons without observing the law of conservation of momentum inside the electron–phonon system, the effectiveness of this kind of interaction being much greater for the case of liquid metals and metallizing semiconductors. Reference 27 points to another type of possible non-elastic interactions in liquid conductors. It is noted that in the case of the degenerate gas of the carriers there takes place damping of one-particle excitations due to non-elastic collisions taking place in the electron–electron system. This is also a result of inaction of the law of conservation of momentum in disordered systems. Therefore we believe that in metallizing semiconductors of the type of lead telluride there develop phonon–electron and electron–electron non-elastic processes of dispersion, whose action is non-equivalent in the presence of a magnetic field and temperature gradient, as a result of which Lorentz experimental number is smaller than the theoretical one. It should be also noted in this connection that the explanation of the negative deviation from Wiedemann-Franz law requires a qualitatively new approach to the character of the change of the energy spectrum of the carriers during melting according to the semiconductor-metal type.

The point is that the probability of non-elastic collisions is considerably great only in case the metallization is accompanied by a much greater growth in the number of free states than the change in the number of free carriers during the destruction of the system of atomic bonds. It is possible to assume that such expansion of the phase space may take place due to the appearance of additional states within the boundaries of the former forbidden band. In case the process of metallization is interpreted by the conventional method, i.e. as a result of a considerable increase in the concentration of free carriers, then Pauli principle will exclude interactions in the degenerate electron gas accompanied by a great loss of energy.

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