THERMOPHYSICAL PROPERTIES OF POLYVALENT METALS AND THEIR ALLOYS IN THE SOLID AND LIQUID STATES

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Resistivity, thermal conductivity, and ultrasound velocity for the metals of the third group, namely, gallium, indium, and thallium are given in a temperature range from 300 to 1000°K as well as resistivity and thermal conductivity of indium–thallium and thallium–tin alloy systems in wide temperature and concentration ranges.

This article presents the results of an experimental study of the electrical resistivity, thermal conductivity, and velocity of ultrasound in third-group metals gallium, indium, and thallium and indium–thallium and thallium–tin alloys in the temperature range 300-1000°K. The electrical resistivity (ρ) of the metals and alloys was determined by the four-probe compensation method on a unit described in detail in [1]. The standard deviation of the resistivity measurements, with a confidence coefficient of 0.95, was no more than 0.5%.

Thermal conductivity (λ) was measured on a unit [2] combining stationary and relative variants of the well-known plane-layer method. An analysis of the errors showed that their limiting value changed from 3.5 to 5% for the absolute method and from 4.5 to 7.3% for the relative method within the working temperature range.

The ultrasonic velocity of sound (C) was determined by the method of phase comparison [3], based on observation of the interference of ultrasonic pulses that traveled different paths in the specimen. The unit consists of an electronic block, a cell, and a system for ensuring homogeneity and measuring temperature. The electronic part of the unit is similar to that described in [4,5]. To automate the measurements, the electronic block also contains an extreme regulator controlled by a high-frequency generator. The regulator maintains the amplitudes of interference pulses at a minimum level. The output voltage of the regulator, proportional to C, is recorded on a recorder simultaneously with the signal from the thermocouples. A cross section of the cell is shown in Fig. 1. Specimen 1 is poured into the volume formed by the ring 2 (the height of which was calibrated) and the ends of the waveguide 3 and reflector 4. The ring is compressed by the ends of the waveguide. The bottom end of the waveguide is screwed into the water cooler 8 of a vacuum chamber with a high-frequency lead. Specimen temperature is increased by means of base heater 6. The uniformity of the specimen and waveguide temperature fields is assured by adjusting the power of heaters 7 and 5 with VRT-3 regulators in accordance with signals from differential thermocouples 9 and 10. Temperature was measured with three Chromel–Alumel thermocouples with a measurement error of 0.15, 0.3, and 0.8° at 500, 700, and 1000°K, respectively. The cell is made of steel 12Kh18N9T. The systematic and random errors were analyzed in accordance with the recommendations in [6,7]. Maximum measurement error was 0.1-0.2% at a probability of 0.95. After achieving stable acoustic contact, the unit has a sensitivity of $\pm 5 \cdot 10^{-5}$. The specimens were degassed in quartz ampoules at 1100°K under a vacuum of $\sim 6 \cdot 10^{-3}$ Pa before being driven into the working volume under pressure by high-purity helium.

The measurements of ρ, λ, and C were made in an inert-gas medium at an excess pressure of 1500-4000 Pa.

Electrical resistivity has been studied fairly well for gallium [8-19] and indium [8-12, 20-24], but there has been relatively little study of the resistivity of thallium [1,8-10,20]. According to all studies, the temperature dependence of the resistivity of indium and thallium is linear, while opinion is divided on this question with respect to gallium. The values of electrical resistivity we obtained for gallium in the range 302.9-1000°K from

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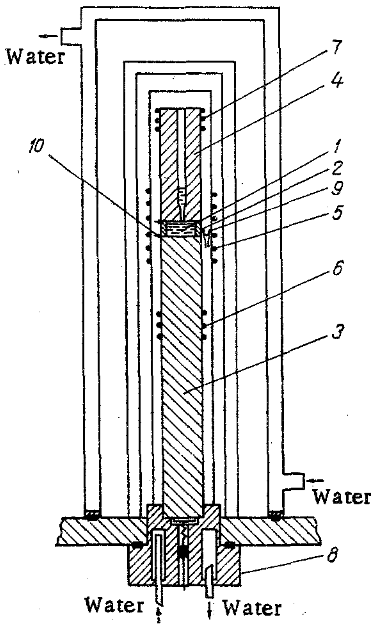

Fig. 1. Schematic of the experimental setup cell for ultrasound velocity measurements.

careful measurements and which we analyzed by the least-squares method are approximated by the equation

$$\rho = (19.51 \pm 0.6) + (2.159 \pm 0.08)\cdot 10^{-2}T - (2.693 \pm 0.104)\cdot 10^{-6}T^2 (10^{-8}\ \Omega\cdot\mathrm{m}).$$

The fairly large number of investigations devoted to the electrical resistivity of gallium, indium, and thallium allows us to generalize the available data for each metal within the temperature range T_{ml}–1000°K. The aggregate of data of different authors was analyzed as a group of series of measurements of the same quantity using the well-known formulas in [7] on electronic digital computer ODRA-1204. Statistical weights were assigned on the basis of the errors cited by the authors and an analysis of the methods they used. Polynomials corresponding to the mean values were obtained as a result of the statistical analysis and are shown in Table 1.

The thermal conductivity of liquid gallium and indium has been the subject of repeated study. However, the results of investigations of gallium [25-29] and indium [25,30] indicate that there is substantial disagreement between authors with respect to both absolute value and the value of the temperature coefficient. These discrepancies are related to the difficulties of conducting high-temperature experiments and, so, to methodological errors [31,7]. Table 1 shows the results of our studies of the thermal conductivities of gallium, indium, and thallium, since statistical analysis of the available data is invalidated by the nonuniformity of the group of series.

The velocity of ultrasound in extremely pure 19–3 indium decreases linearly with temperature from T_{ml} + 0.05 to 1000°K. Table 1 shows the corresponding polynomial obtained by least squares analysis of the empirical data and by statistical analysis of the data in [32-37] using the method in [7]. Our data agree with the recommended data in terms of both absolute value and temperature derivative. The velocity of ultrasound in liquid indium is linear up to the freezing point, while in liquid gallium (Gl-00) its dependence on temperature is nonlinear within the range 410-700°K. Thus, the results can be approximated by three line segments. The corresponding polynomials are given in Table 1. The changes in the temperature derivative at the points of inflection are +0.036 ± 0.004 and +0.022 ± 0.006. Our data agree with respect to absolute value and the presence of nonlinearity with the results in [35]. The results in [36] agree with our data and the data in [35] in terms of absolute value, but the investigators here did not observe any departure from linearity in the temperature dependence of sonic velocity. The data in [38] is 3% higher than ours. The temperature dependence of the velocity of sound in gallium does not deviate from linearity by more than 0.05 m/sec in the course of the transition of gallium to the supercooled state.

TABLE 1. Values of Velocity of Ultrasound and Electrical and Thermal Conductivity for Gallium, Indium, and Thallium

Metal	Property	Polynomial	Temp. range, °K	Remarks
Ga	$\rho \cdot 10^8$, $\Omega \cdot$m	$(25{,}85 \pm 0{,}05) + (1{,}914 \pm 0{,}01)10^{-2}(T - 302{,}9)$	302,9—1000	Av. result
	λ, W/m·°K	$(7{,}6 \pm 0{,}4) + (7{,}92 \pm 1)10^{-2}T - (2{,}6 \pm 1)10^{-5}T^2$	310—800	Our result
	C, m/sec	$(2869{,}8 \mp 5) - (0{,}210 \pm 0{,}003)(T - 302{,}9)$	302,9—373	»
	C, m/sec	$(2855{,}0 \mp 5) - (0{,}246 \mp 0{,}003)(T - 373)$	373—493	»
	C, m/sec	$(2825{,}5 \mp 5) - (0{,}268 \mp 0{,}005)(T - 493)$	493—700	»
In	$\rho \cdot 10^8$, $\Omega \cdot$m	$(32{,}38 \pm 0{,}05) + (2{,}52 \pm 0{,}01)10^{-2}(T - 429{,}8)$	429,8—1000	Av. result
	λ, W/m·°K	$(31{,}5 \pm 1{,}6) + (4{,}28 \pm 0{,}04)10^{-2}(T - 440)$	440—800	Our result
	C, m/sec	$(2312 \mp 4) - (0{,}300 \mp 0{,}003)(T - 429{,}8)$	429,8—1000	»
	C, m/sec	$2313 \mp 1{,}5) - (0{,}299 \pm 0{,}0015)(T - 429{,}8)$	429,8—1000	Av. result
Tl	$\rho \cdot 10^8$, $\Omega \cdot$m	$(76{,}48 \pm 0{,}08) + (2{,}78 \pm 0{,}03)10^{-2}(T - 577)$	577—1000	Av. result
	λ, W/m·°K	$(18{,}4 \pm 0{,}9) + (2{,}66 \pm 0{,}03)10^{-2}(T - 587)$	587—800	Our result
	C, m/sec	$(1659{,}6 \pm 3{,}2) - (0{,}231 \pm 0{,}1)(T - 577)$	577—1120	[32,35]

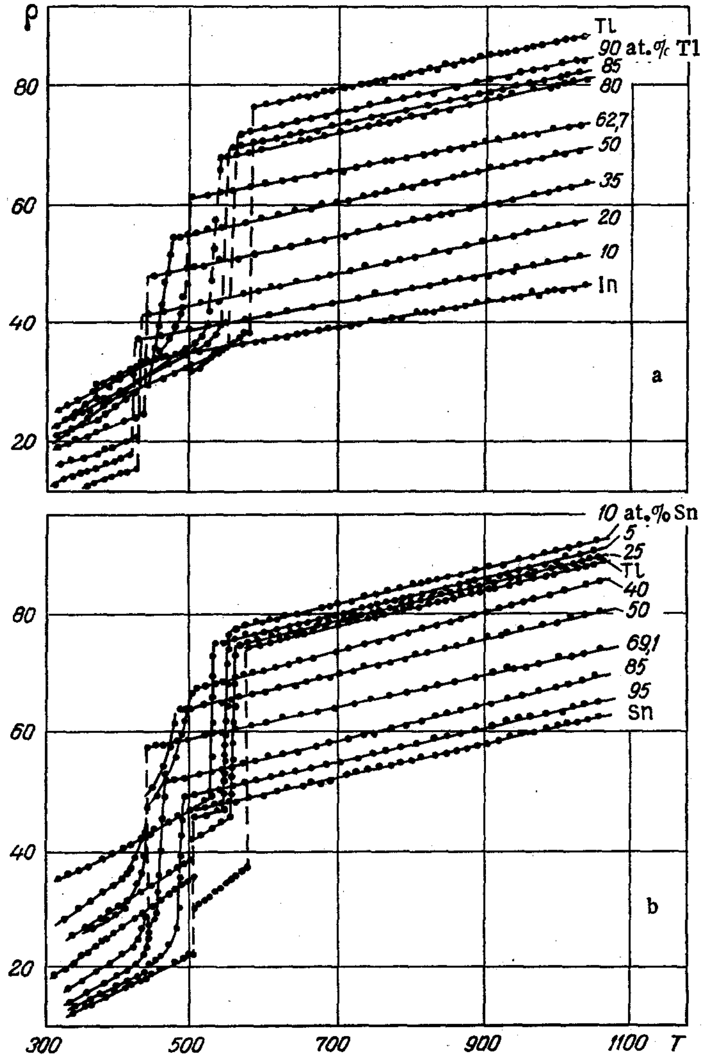

Fig. 2. Resistivity ρ polytherms for indium–thallium (a) and thallium–tin (b) alloy systems.

Very few studies have been devoted to systematic investigation of the thermophysical properties of thallium alloys within a wide range of temperatures and concentrations. The

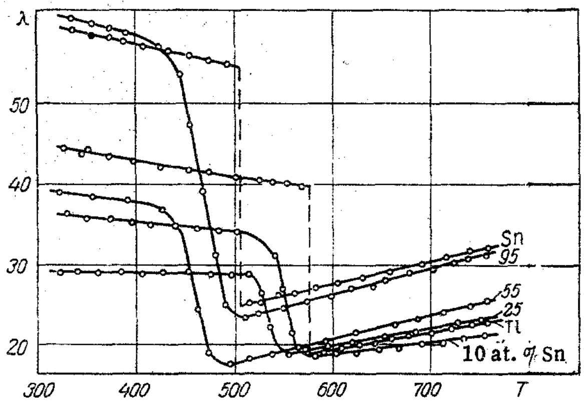

Fig. 3. Thermal conductivity λ polytherms for thallium–tin alloy system.

electrical resistivity of alloys of the indium–thallium system was studied in [20,39] and in [40,41] but there is no data for the thallium–tin system. The available data on the resistivity of melts of the indium–thallium system is highly contradictory. In [39] the resistivity isotherms anomalously deviate from the parabolic dependence observed earlier in [20]. According to our investigations, the isotherm of the resistivity of this system in the liquid state, plotted from the results shown in Fig. 2a, deviates only slightly from an additive curve (∿4%) with a positive deviation and is in agreement with the result obtained in [20]; the maximum deviation of the isotherm in the solid state in the positive direction is 37%, corresponding to a concentration of 60-70 at. % Tl. This agrees well with the data in [39]. The similar behavior of the solid-state isotherms in [39] is evidently related to the fact that specimens with a high vapor pressure were studied in a vacuum. Figures 2b and 3 show our data for the coefficients of thermal and electrical conductivity in the solid and liquid states. We should emphasize the full correlation of these properties. The Wiedemann–Franz law is observed for the investigated alloys in the liquid phase with an accuracy equal to the total experimental error. The isotherms of these properties are close to parabolas. The maximum deviation of the resistivity isotherm from an additive function is about 60% for the solid state and about 6% for the liquid state and corresponds to a concentration Tl + 25 at. % Sn.

The deviation of the isotherms of the kinetic properties from linearity for the investigated systems in both the solid and liquid states depends mainly on the degree of nonideality of the solutions. An increase in the volume of the alloys during melting leads to weakening of individual features of the interatomic bonds of the constituents, so that the liquid-state isotherms deviate less from additive values than isotherms for the solid state. The phase boundaries in the solid state on polytherms of resistivity, denoted by breaks and points of inflection, are in agreement with the constitutional diagrams shown in [42] in the region rich in thallium, but do not agree with the diagram recommended in [43]. As we noted earlier [44], this fact can evidently explain the relatively strong dependence of the structure of tin-base alloys on heat treatment.

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INFLUENCE OF QUASILOCAL OSCILLATIONS ON THE THERMAL EXPANSION AND SPECIFIC HEAT OF METALS AT LOW TEMPERATURES

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The influence of heavy impurity atoms on the thermal expansion and specific heat of magnesium, aluminum, and titanium (4-300°K) is studied. The possibility of predicting the mentioned thermophysical properties of such systems is examined.

An important problem of modern material science is the prediction of the thermophysical properties of structural materials and the development of appropriate technological recommendations. In a number of cases such predictions can be made for weak solid solutions on the basis of modern conceptions of the role of the mass of foreign atoms and of the perturbations of interatomic binding forces. Systems with heavy impurity atoms are of interest since an anomalously high rise in the specific heat and thermal expansion can be observed in this case at low temperatures [1-7] because of the occurrence of quasilocal vibrations (QLV). Such impurities are often contained in light metals and alloys used in cryogenic engineering, which stimulates the study of the thermophysical properties of similar systems. Unfortunately, the known literature data for many engineering alloys cannot be compared to computations because of their poor accuracy, and therefore, cannot be analyzed from the viewpoint mentioned; specially designed experiments are needed.

The influence of heavy impurity atoms resulting in the occurrence of QLV on the specific heat and thermal expansion of light metals such as magnesium, aluminum, and titanium is studied in this paper. The problem of obtaining experimental results and comparing them to results of theoretical computations to clarify the possibility, in principle, of predicting

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