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AN ANOMALY IN THE KINETIC PROPERTIES OF TIN IN THE POLYMORPHIC PHASE TRANSITION REGION

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Experimental data are presented on the resistivity and thermo-emf of tin over the temperature range −183 to 700°C, on thermal conductivity from −183 to + 300°C, and on the speed of ultrasound from 20 to 400°C. Anomalies appear in the temperature curves corresponding to polymorphic transitions in the tin.

Study of the thermophysical properties of tin is of interest both for the development of theory and for practical goals.

Three modifications of tin in the solid state have been established: gray tin, α-Sn; white, β-tin, and γ-tin, which may transform to each other at certain temperatures according to the pattern α-Sn $\rightleftharpoons$ β-Sn $\rightleftharpoons$ γ-Sn $\rightleftharpoons$ liquid tin. Of these modifications, gray tin has semiconductor properties. It crystallizes in a diamond lattice and is stable below 13.2°C. Above this temperature α-Sn transforms to β-Sn, which crystallizes in a tetragonal lattice. The highest α- and β-tin conversion rate occurs at −40°C. Upon heating of white tin above 161°C it transforms to the rhombic modification, γ-tin.

The three modifications are characterized by different densities: α, 5.846; β, 7.298, and γ, 6.600 g/cm^3.

The structure of liquid tin has been examined in many studies; their results indicate that in tin an incomplete transformation of directed bond to metallic occurs, with conversion of the crystalline structure into one of the structures characteristic of metallic bonding – bcc or cph. Khrushchev [1] explains the presence of lateral intensity maxima in the intensity curves and radial distribution function as the result of directed bonds near the crystallization point. These maxima disappear with increase in temperature. After analysis of various experimental data Turakawa et al. [2] proposed that liquid tin near the melting point is a system of ordered regions corresponding to gray tin structure distributed in a metallic structure. Conductivity and viscosity studies [3] have shown that tin has an anomaly in the resistance temperature coefficient at 520°C; this was related to a change in atomic packing, i.e., to a change in close order.

A number of studies [3-10] have considered the kinetic properties of tin above room temperature. It follows from them that with the exception of [3, 7] the temperature curves of the various kinetic properties show no singular points corresponding to structural transformations of the various modifications in tin. However, the available information on the kinetic properties of tin at low temperature is very limited.

The present study is dedicated to an investigation of the thermal conductivity, resistivity, thermo-emf, and speed of ultrasound in Sn-000 over a wide temperature interval encompassing both the solid and liquid phase.

Electrical Resistance. The experimentally determined temperature dependence of electrical resistivity in tin is shown in Fig. 1. Measurements were made by the four-probe method with an accuracy of 1%. The tin transformations noted above were found from changes in the temperature coefficient of resistivity in the curve $\rho = f(t)$ at temperatures of 50, 100, and 520°C.

Table 1 presents values of $d\rho/dt$ corresponding to the various modifications. The temperature intervals are accurate to ±10°C.

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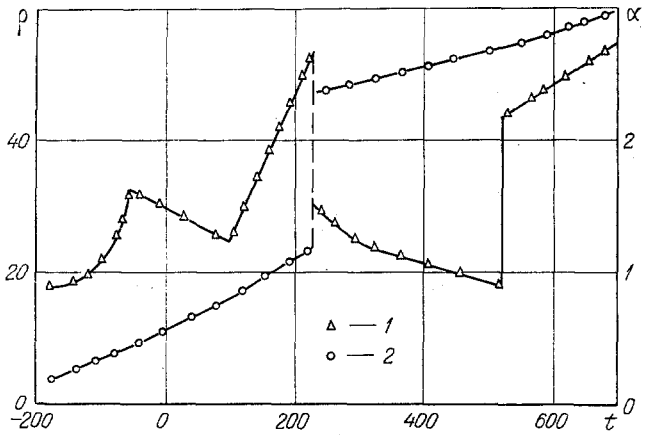

Fig. 1. Electrical resistivity and thermo-emf of tin vs temperature: 1) α; 2) ρ. t, °C; ρ, $\mu\Omega \cdot$cm; α, μV/deg.

The lowest value of the temperature coefficient, corresponding to α-Sn, is evidently connected with the semiconductor property of that phase.

Upon transition to the liquid phase the resistivity of tin increases by a factor of two, while the temperature coefficient of ρ decreases by approximately a factor of two.

As was indicated above, diffraction studies have established that close order in liquid tin is realized by a combination of the two types gray tin and white tin. Above 520°C the coordination number takes on a new value. Correspondingly, the change in $d\rho/dt$ is related to a change in close order, i.e., of the chemical nature of the atoms, the geometry of their disposition, and the absolute distance between them, all of which together determine the character of the bonds in the material.

The temperature coefficients of resistivity are positive in sign over the entire temperature interval.

Thermo-emf (α). The thermo-emf was measured with two pieces of equipment. With the first, designed for low-temperature studies of α, the emf was measured relative to copper with temperature determined by copper – Constantan thermocouples. To calculate the absolute values data on the absolute thermo-emf of copper from [13] was used. With the second apparatus, designed for high temperatures from room to 700°C, the thermo-emf was measured relative to Alumel, with temperature measurement by Chromel – Alumel thermocouples. Absolute values of thermo-emf obtained with both devices were easily reproducible in the temperature range 20-150°C. The measurement uncertainty α was no more than 3.5%. The data agree well with [9, 12] in the range 232-350°C.

Figure 1 shows curves of $\alpha = f(t)$, where in both solid and liquid states the singular points are distinguished by a change in the temperature coefficient $d\alpha/dt$. For the α and γ phases $d\alpha/dt$ is positive in sign, but is negative for the β phase. In the liquid state up to 520°C $d\alpha/dt$ is negative, and above this temperature it is positive.

Regel' [8] has related the low absolute value of α in metals such as Cd, Zn, Pb, Hg, In, and Sn, as compared to the thermo-emf's of metals of the first group, to a mixed electron-hole conduction mechanism.

Thermal Conductivity (λ). The thermal conductivity of liquid tin has been studied thoroughly. Data was presented in the review [10], with scattering near the melting point of ~10%, while the temperature coefficients in the liquid phase differ significantly from each other, even being of opposite sign. Data on the thermal conductivity of tin in the solid state is very sparse in the literature, and the scattering is greater than 20%. At low temperatures thermal conductivity has not been studied at all.

TABLE 1. $\partial\rho/\partial t$ of Tin vs Temperature

$\partial\rho/\partial t$, $\mu\Omega \cdot$cm$\cdot$deg	Temperature interval, °C				
	from −183 to −50	from −50 to +100	from +100 to 232	from 232 to 520	from 520 to 700
	0,04227	0,05133	0,05770	0,02500	0,02780

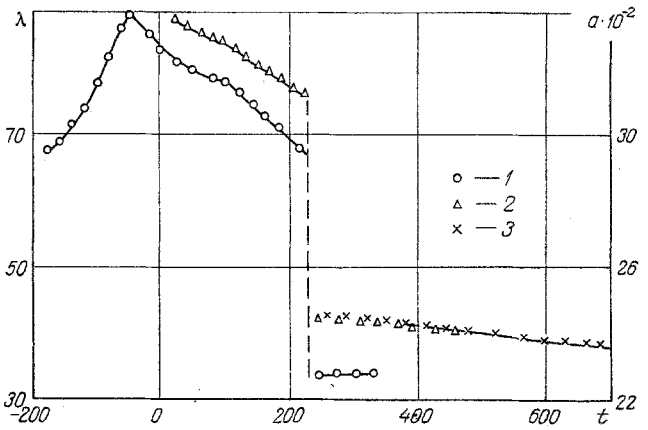

Fig. 2. Thermal conductivity and speed of sound in tin vs temperature: 1) λ; 2) a; 3) a [16]. t, °C; λ, W/m·deg; $a \cdot 10^{-2}$, m/sec.

The present study investigated the thermal conductivity of tin over the temperature range −183 to +300°C, encompassing the entire polymorphic transformation range. Measurements were performed by the absolute stationary plane layer method. The heater was located between two identical specimens with section diameter of 10 mm. Temperature difference in the specimen was measured by four copper – Constantan thermocouples 0.15 mm in diameter attached to the specimen at 10-mm distances. The specimen was placed in a preprocessed Teflon cylinder with inner diameter of 10 mm and outer diameter of 12 mm. Coolers were installed on both sides of the specimen. The entire assemblage was placed in a hermetically sealed cylinder of 1Kh18N9T stainless steel with inner diameter of 14 mm and outer diameter of 17 mm. Such an arrangement permits placing the experimental apparatus in either a Dewar flask filled with various liquids, or a furnace, or within a magnetic field. Before measurements the chamber was evacuated to 10^{-4} mm Hg.

The total maximum uncertainty in the measurements is composed of the uncertainty in determination of geometric dimensions (±1%), in temperature difference determination (±1.9%), quantity of heat transmitted (±1.8%), with the sum reaching ±4.7%.

Figure 2 shows a curve of the temperature dependence of λ for tin. At −50°C (conversion of α- to β-tin) $d\lambda/dt$ changes value and sign, while at 100° (β – γ transformation) only the value of the temperature coefficient changes. Upon melting, the thermal conductivity decreases by a factor of 1.9, and $d\lambda/dt$ changes sign from negative in the solid to positive in the liquid. Experimental values of λ and the value of the temperature coefficient for tin in the liquid phase obtained in this study agree satisfactorily with the data of [11].

On the basis of the experimental data obtained on thermal conductivity and resistivity the Lorentz number was calculated for various temperatures and is presented in Table 2.

Large values of Lorentz number as compared to theoretical values for metals are apparently related to the role of phonon thermal conductivity. The participation of phonons in heat transfer for the various modifications of tin differs. Above 100°C the Lorentz number decreases monotonically with increase in temperature, but changes discontinuously upon melting. In the liquid phase L also has a negative temperature coefficient. According to [14], due to an increase in disorder of ion location with increase in temperature the role of phonon liquid scattering of electrons increases, which leads to a growth in elastic scattering of the electron conductivity and a reduction in the Lorentz number.

Speed of Ultrasound. The literature offers little information on the temperature dependence of the speed of ultrasound in solid tin, while the dependence $a = f(t)$ in liquid tin was investigated in several works. Results

TABLE 2. Lorentz Number vs Temperature for Tin

$T°$, C	−150	−100	−50	0	+50	+150	+250	+300
$L, V^2/deg$	2,56	2,98	3,40	3,49	3,50	3,48	3,04	2,93

are shown in reviews [15, 16] and one notes fairly good agreement between the data of various authors.

In Figure 2 are presented curves of the temperature dependence of the speed of ultrasound on temperature for tin over the temperature range from room to 400°C. Measurements were made in the present study by the ultrasound impulse method, with relative accuracy of 0.3%.

Upon transition to the liquid phase a decreases by a factor of 1.27 times, and da/dt maintains a negative value, as in the solid phase.

In [16] it was noted that at 820°K the temperature coefficient of the speed of sound in tin decreases, which is a consequence of structural changes in the liquid tin.

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