NOTATION

T_b, normal boiling point of liquid at atmospheric pressure; n_C, number of carbon atoms in molecule.

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CONDUCTIVITY IN ALLOTROPIC PHASE TRANSITIONS

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A method is given for calculating the resistivity as a function of temperature in the presence of structural phase transitions in solids.

Many studies have been performed [1-3] on the conductivity in the presence of allotropic phase transitions, which is a subject related to the design of critical resistors. However, the basic characteristic, viz., the electrical resistance R as a function of temperature T, has so far been described only by approximation.

Here we present a quantitative theory that employs the initial and final critical conductivities with the heat of phase transition and the temperature range of the transition to calculate the resistance as a function of temperature. Realistic objects are characteristic critical thermistors with structural phase transitions of different kinds: the metal – semiconductor transition in VO_2 [4-8] and the ferroelectric – paraelectric transition in $BaTiO_3$ ceramic [1].

The initial model concepts include the existence of a structurally homogeneous phase below the transition point, which is characterized by a specific conductivity σ_1 and a temperature coefficient of the conductivity α_1.

As the temperature rises, deviations from σ_1 as corrected by α_1 begin to appear at $T = T_i$; in the range from T_i to T_f there is a change in the electrical conductivity, and above T_f there is a structurally homogeneous phase with conductivity σ_2 and temperature coefficient of conductivity α_2.

There is a phase transition in the range T_i-T_f which is due to the difference in chemical potential between the two phases. The new phase arises in the old matrix in the theory of heterogeneous transitions [9], which occurs by nucleation and growth of the new phase. We assume that the major changes in concentration are due to the growth, which occurs at the nuclei. In turn, nucleation is due to heterophase fluctuations. The nucleation probability is related to the particle mobility via the factor $\exp(-U/KT)$, in which U is an activation energy [9]. The overall concentration of such nuclei is proportional to the internal energy of the solid, so the temperature dependence of the concentration tends to run parallel to the temperature dependence of the specific heat.

The activation energy of growth is always less than that for the nucleation, so nucleation is rapidly followed by growth, which transforms the bulk of the material. Nucleation and growth are independent processes resulting from the fluctuations. Growth arises only from fluctuations that exceed the critical level and which occur near the interface between the phases, i.e., near the nuclei. The entropy of activation characterizes the probability of occurrence of a favorable spatial orientation [10].

Therefore, the concentration of nuclei is proportional to the specific heat, while the concentration of the new phase arising by growth is proportional to the entropy change in the transition.

Let m_2 be the volume concentration of the new phase; then we perform a normalization over the temperature range in which the transition occurs to get

$$m_2 = \frac{C_v - C_{v\,i}}{C_{v\,f} - C_{v\,i}} \frac{\Delta S - \Delta S_i}{\Delta S_f - \Delta S_i}. \tag{1}$$

The first cofactor defines the probability of nucleation, while the second defines the growth probability. The product of the probabilities for these independent events defines the probability that the volume will go from one phase to the other. This probability, expressed as a fraction, may be described as the proportion of the volume that has gone over to the new state.

Therefore, the model is based on the following axiom: the proportion of the volume converted to one phase from another in an allotropic transition is equal to the probability of formation of the new phase expressed as a fraction.

The temperature course of C_V may be derived from the Einstein – Nernst – Lindemann expression [10]:

$$C_v = \frac{3}{2} R' \left[\frac{\left(\exp \frac{\Theta}{T} \right) \left(\frac{\Theta}{T} \right)^2}{\left(\exp \frac{\Theta}{T} - 1 \right)^2} + \frac{\left(\exp \frac{\Theta}{2T} \right) \left(\frac{\Theta}{2T} \right)^2}{\left(\exp \frac{\Theta}{2T} - 1 \right)^2} \right]. \tag{2}$$

The characteristic temperature for the substance is defined by $\Theta = 134.4\sqrt{T_s/AV^{2/3}}$, where V is the molar volume, A is the molecular mass, and T_s is the melting point. The value of ΔS may be calculated from the heat of transition $\Delta H = T\Delta S$.

From (1) we can calculate m_2 as a function of temperature, which can then be used with the theory of generalized conduction [17-19] to relate the electrical conductivity to temperature. For this purpose we need an analytic expression for $\sigma = \sigma(m_2)$.

The most general description for the structure change in a binary heterogeneous system is in terms of the concentrations m_2 and $m_1 = (1 - m_2)$; the theory indicates that the second phase (volume concentration m_2) initially forms isolated and randomly disposed clusters in the continuous first phase, which grow to some value $m_2 < m_c$ while remaining isolated (Fig. 1a, b). At concentrations $m_2 = m_c$ and above, the clusters combine into a single unbounded cluster, and values $m_2 > m_c$ result in increase in the volume of this cluster (Fig. 1c) until $m_2 = 1$. If the conductivities are very different, e.g., σ_m metallic and σ_d dielectric ($\nu_m = \sigma_d/\sigma_m = 0$), then there is a discontinuity in the effective conductivity σ as a function of m_2 (conduction jump) at $m_2 = m_m = m_c$, viz., $\sigma = 0$ for $m_c \leq 0$, whereas for $m_m > m_c$ we get $\sigma \neq 0$. The value of m_c is then called the threshold and indicates what value of m_m is required to produce an infinite cluster of the conducting component. Computer simulation of the random distribution in a three-dimensional binary heterogeneous system has been combined with laboratory experiment to show that m_c fits a random distribution and is on the average $m_c = 0.15 \pm 0.03$ [20, 21].
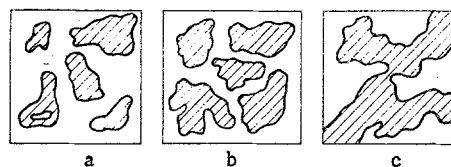

Fig. 1. Structure of a binary heterogeneous system for various values of the concentration: a) nucleation of new phase (isolated clusters); b) growth of nuclei (isolated clusters); c) formation of unbounded cluster.
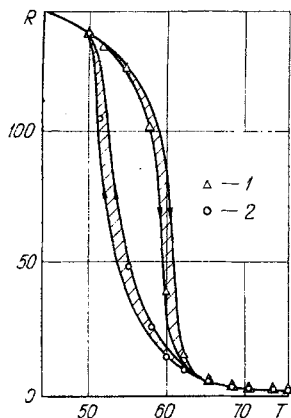
Fig. 2. Electrical resistance as a function of temperature for VO_2: 1) values observed with the temperature increasing; 2) values observed with the temperature decreasing [1]. The solid lines are theoretical values for $0.12 \leq m_C \leq 0.18$. R, Ω; T, °C.

Analytical description of the conductivity in such a binary system in the presence of a jump at $m_2 = m_C$ requires a description of the cluster topology. An analytic description has been suggested [19] for the topology, and this has been used in a method of calculating σ for a binary heterogeneous system with any value of $\nu = \sigma_d/\sigma_m$:

$$\sigma/\sigma_m = F_1 + \nu \left[\frac{\Delta F}{1 - (1 - \nu)\, l_2} + 2 \frac{F_3}{1 - (1 - \nu)\, l_1} + F_4 \right]. \tag{3}$$

Here the symbols are: $F_1 = [(m_m - m_c)/(1 - m_c)]^{1.6}$; $F_2 = m_c^{2/3}$; $l_1 = \sqrt{F_1}$; $F_3 = (1 - l_2)l_1$; $F_4 = 1 - F_2 - 2F_3$, and the following inequalities must be met:

if $F_2 > F_1$, then

$$\Delta F = F_2 - F_1, \quad l_2 = m_c^{1/3}; \tag{4}$$

if $F_2 \leq F_1$, then

$$\Delta F = 0, \quad l_2 = l_1 = \sqrt{F_1}. \tag{5}$$

The first case corresponds physically to the formation of an unbounded cluster, whereas the second corresponds to the formation of closed inclusions, i.e., isolated clusters.

Then (1)-(5) allows one to perform calculations on the conductivity in allotropic phase transitions. We now consider the electrical resistivity as a function of temperature for various materials with structural transitions. Figure 2 (solid lines) shows results along with experimental data (points) for a device using the metal–semiconductor transition in VO_2. When $\rho = \sigma^{-1}$ is calculated from (3)-(5), the value of the concentration corresponding to the discontinuity occurs in the range $0.12 \leq m_C \leq 0.18$, which results in the hatched region shown in Fig. 2. The initial data were as follows: conductivity of the metal component $\sigma_m = 4.65\ \Omega^{-1}$, of the semiconductor component $\sigma_d = 7.4 \cdot 10^{-3}\ \Omega^{-1}$, and the parameters appearing in (2) and (3) were V = $36.9 \cdot 10^{-6}\ m^3$, A = 83, $T_s = 1818°K$, $\Delta H = 4.3$ J/kmole, $T_i = 323°K$, $T_f = 348°K$ [22].

It follows from Fig. 2 that R = R(T) shows hysteresis: the concentrations m_2' and m_2'' of the metallic phase are different at a given temperature in accordance with whether the temperature is increasing or decreasing.
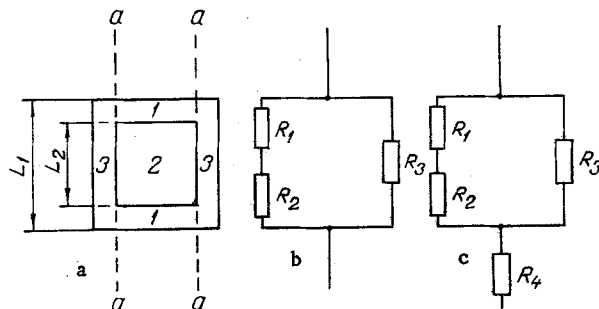

Fig. 3. Calculation of the effective conductivity of a ceramic grain: a) grain model; b) equivalent circuit for conduction before phase transition; c) the same after phase transition.
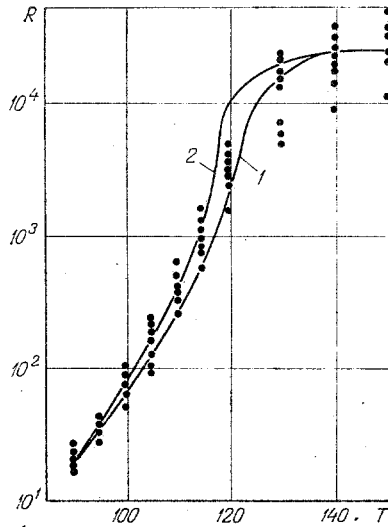
Fig. 4. Electrical resistance of $BaTiO_3$ as a function of temperature (the points are from experiment and the solid lines are calculations for 0.12 (1) $\le m_c \le 0.18$ (2). R, Ω; T, °C.

Hysteresis is implied by the structure of (1), which we write for the forward and reverse branches of the $R = R(T)$ curve on the basis that the initial temperature T_i and the final temperature T_f change places, as do the corresponding values of C_V and ΔS. The concentrations on the forward and reverse branches must be calculated from

$$m_2' = \frac{C_v - C_{vi}}{C_{vf} - C_{vi}} \frac{\Delta S - \Delta S_i}{\Delta S_f - \Delta S_i}, \quad m_2'' = \frac{C_v - C_{vf}}{C_{vi} - C_{vf}} \frac{\Delta S - \Delta S_f}{\Delta S_i - \Delta S_f}. \tag{6}$$

It follows from (6) that $m_2' \neq m_2''$ and that (1) is not invariant under the sense of the process, i.e., one always expects hysteresis in an allotropic phase transition, whose exact extent is dependent on the order of magnitude of the heat of the phase transition, and which in certain cases may be suppressed by other processes. For example, percolation effects ($m_c = 0.15 \pm 0.03$) lead to some spread in the forward and reverse branches, which may then overlap, in which case the hysteresis is not clearly seen. Further, there may be other physical processes that suppress the hysteresis. This is clearly seen by the $R = R(T)$ relation for $BaTiO_3$ semiconductor ceramic near the ferroelectric – paraelectric phase transition. In this transition, there is an anomalous increase in the specific resistance of the material. This has been ascribed to processes occurring at grain boundaries and at the margins of domains, where double electrical layers arise, which determine the conductivity of the material [11-14]. The charges accumulated in these double layers determine the potential barriers to the conduction electrons and themselves are dependent on the state of the $BaTiO_3$ crystals forming the cores of the grains [15, 16]. $BaTiO_3$ is ferroelectric below the transition temperature, but paraelectric above it, while the transition is accompanied by an increase in height in the potential barriers at the grain boundaries [11-13]. A grain of semiconductor ceramic may be represented as a core of material surrounded by a shell having a different conductivity. The potential barriers between grains are low in the ferroelectric state, and the conductivity of the ceramic is governed by that of the cores and by that of the surrounding layers. The potential barriers become much higher when the ferroelectric – paraelectric transition occurs, and therefore the resistivity of the paraelectric state is much higher on account of the contact resistances between the grains (resistance R_4 in Fig. 3c).

A mode of cube-in-cube type can be used to a good approximation to calculate the effective resistance. We split up the cubes with planes $a - a$ impermeable to the current lines as shown in Fig. 3a and denote the resistance of the core by R_1 and that of the boundary layers by R_2 and R_3; the mode of connection of the latter is shown in Fig. 3b. The resistances R_i of the regions $i = 1, 2, 3$ are defined by simple formulas:

$$R_1 = \rho_1 \frac{L_1 - L_2}{L_2^2}, \quad R_2 = \rho_2 \frac{L_2}{L_2^2}, \quad R_3 = \rho_1 \frac{L_1}{L_1^2 - L_2^2}. \tag{7}$$

The specific resistance ρ_i and length L_i for the current lines are chosen in accordance with [13, 14]. The conductivity is represented by the equivalent circuit of Fig. 3c, which incorporates the potential barriers at the grain boundaries, after the transition point, where the resistance of a barrier is [1]

$$R_4 = \rho_4 \frac{L_b}{L_2^2}, \quad \rho_4 = C \exp{(U/KT)}. \tag{8}$$

As the conductivities of the individual grains are known in the two states, we can discuss the conduction through the thermoresistor. In the transition range, the material is a two-component mixture with a random distribution of the components. Below T_i, the material is homogeneous and has the high conductivity σ_m, while the phase transition finishes at T_f, where the material goes over completely to the new phase having the much reduced conductivity $\sigma_d \ll \sigma_m$. We have seen above that the continuous component of conductivity σ_d produces isolated clusters of conductivity σ_m, and then these clusters become an unbounded cluster as m_m increases. Any further increase in m_m merely increases the volume occupied by the unbounded cluster of conductivity σ_m.

Formulas (1)-(8) are used to calculate $R = \sigma^{-1}$ for a $BaTiO_3$ thermistor on the basis of the following parameters [10, 13, 14]: the conductivities of the components are $\sigma_m = 4 \cdot 10^{-2} \, \Omega^{-1}$, $\sigma_d = 4 \cdot 10^{-5} \, \Omega^{-1}$, while the parameters appearing in (2) and (3) are $V = 39.7 \cdot 10^{-6} \, m^3$, $A = 233$, $T_s = 1600°K$, and the heat of transformation in the phase transition is $\Delta H = 0.15$ J/kmole, $T_i = 363°K$, $T_f = 423°K$. Figure 4 shows theoretical results on the conductivity of a $BaTiO_3$ semiconductor device. The measured values are shown as points, while the theoretical values are shown as solid lines, which together form a certain region corresponding to the range of concentrations $0.12 \leq m_c \leq 0.18$. Here the percolation effect is accompanied by a process associated with the above phenomena at the grain contacts, which suppresses the appearance of hysteresis in $R = R(T)$. However, a study of the structure of $BaTiO_3$ in the phase transition has shown that there is temperature hysteresis [15].

Comparison of Figs. 2 and 4 shows satisfactory agreement between the observed and theoretical results, and therefore this method can be used in calculating the electrical conductivity as a function of temperature for structural phase transitions in solids.

NOTATION

T, T_i, T_f, and T_s, current, initial, final (transition), and fusion temperatures of the material, respectively; R, resistivity; σ, conductivity; α, thermal diffusivity; C_V, specific heat at constant volume; ΔS, entropy change in phase transition; ΔH, heat of phase transition; R', universal gas constant; m, volume concentration; L_b, U, width and height of the potential barrier. Subscripts: i, initial value; f, final value; m, metal; d, dielectric; c, threshold of percolation.

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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 ρ = f(t) at temperatures of 50, 100, and 520°C.

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