HIGH-TEMPERATURE INVESTIGATIONS OF THE THERMAL PROPERTIES OF SOLIDS

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This paper is a brief survey of research conducted in recent years in the molecular physics department of the Moscow University physics faculty in combination with the geothermal laboratory of the geophysics branch of the same faculty. The researches of the molecular physics department are devoted to the study of the thermal properties of solid and liquid metals in the high temperature range, and those of the geothermal laboratory to high-temperature properties of mountain rocks and minerals. Hence, the research of both groups, carried out in close contact, includes an extensive circle of objects of investigation such as solid infusible metals, solid and liquid phases of relatively fusible metals, solid dielectrics, and semiconductors including refractories, mountain rocks, and minerals.

In speaking of the purposes and importance of the complex of investigations under consideration, it is necessary to isolate the following aspects:

1) the study of high-temperature properties of solid metals and dielectrics in the light of problems of solid-state physics;

2) the study of the behavior of solid metals and semiconductors in the liquid-phase domain;

3) the investigation of the properties of mountain rocks;

4) the applied value of the investigations conducted.

In the first of these aspects we have in mind the study of the specifics of the solid-state domain characterized by comparatively high values of the ratio between the absolute temperature and the characteristic Debye temperature, i.e., the domain of states which cannot be studied by dealing with fusible substances. Among the specific problems of such investigations are:

1) investigations of the specific heat of solids in connection with an enquiry into the role of anharmonicity of the lattice oscillations, the electron contribution to the specific heat of metals and semiconductors, and the influence of the process of thermal vacancy formation;

2) the study of the temperature conductivity of solids in connection with new researches of A. S. Predvoditelev;

3) the study of the heat conductivity of dielectrics and semiconductors in connection with an enquiry into the mechanism of lattice heat conductivity in the high temperature range, the role of radiation transport, and the electron contribution to heat conductivity;

4) the investigation of lattice heat conductivity in metal bodies and the specifics of electron transport.

The second of the isolated aspects of investigation is associated with the activity of the laboratory of the physics of fluids, which is concerned with the study of the nature of thermal motion in liquid media.

The purpose in conducting joint investigations of the properties of solid and liquid media is to compare the appearance of thermal motion in these media.

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The main task in the investigations of the earth's thermals is to study the thermal properties of mountain rock at high temperatures and pressures in order to examine questions of the rate of heat loss by the earth to space and of the thermal evolution of the earth and planets.

Finally, the applied value of the investigations conducted should be emphasized. A study of the properties of solid heat-resistant materials is one of the important tasks of modern thermophysics. With the use of a large quantity of diverse structural materials in the products of new technology, it is entirely necessary to create effective measurement methods and to develop the theoretical and empirical generalizations needed for technological computations.

The aims and tasks of research formulated above comprise a definite, sufficiently extensive program of activity undertaken by the collectives named above.

In the area of studying the properties of solid metals, the first stage of the research, devoted to methodological problems, and to the production of new effective methods of measuring a complex of thermal characteristics, can be regarded, basically, as complete.

The second stage of these investigations, involving the accumulation of experimental material and its systematization, has also been completed sufficiently. Research devoted to the analysis and generalization of the data obtained is presently continuing.

Investigations of the properties of nonmetallic solids were started somewhat later. However, the first, methodological, stage in this research is also close to completion, experimental material is accumulating, and its systematization has been started.

There follows a brief exposition and extension of the investigations performed in the last five years. (The results of researches of the preceding years have appeared more or less completely in the monographs [1-2] and a number of surveys (see [3-5], for example).) Researches performed by the authors in conjunction with aspirants and colleagues of the University, A. V. Arutyunov, S. Atalla, S. N. Banchil, I. N. Makarenko, M. Mebed, G. I. Petrunin, G. F. Tkach, and L. N. Trukhanova, are examined herein.

Let us first consider problems relating to measurement methods.

Measurements of the thermal properties, especially the heat conductivity, in the high temperature range (1000-3000°K) are among the most difficult of measurements.

One of the essential peculiarities of the high temperature range is the large role of radiation heat exchange which is nonlinear with respect to the temperature. Because of this circumstance it is of particular importance to carry out measurements under conditions of small change of temperature; this presents serious difficulties which result in high measurement errors. Not by accident does the great mass of experimental results prove to be contradictory. Research devoted to the development of improved measurement facilities in the area under consideration is entirely necessary.

We found a means to the solution by using a periodic heating mode. The main advantage of applying periodic processes is the huge quantity of information obtained in the experiment. The information sources are the medium temperature fields, the amplitudes of several harmonic components of the temperature fluctuations, and the phase of the fluctuations. The large quantity of information in such experiments permits the realization of complex methods assuring that a whole set of the fundamental thermal characteristics, the heat conductivity, specific heat, temperature conductivity, thermal activity coefficient, will be obtained in our experiment. We shall examine specific research methods based on the use of a fluctuating thermal mode in more detail below, but now we consider one important aspect of the practice of using periodic processes which has been developed recent years. We speak about the peculiarities of periodic heating with a Π-like introduction of power to the sample under investigation. The Π-like periodic modulation is one of the most convenient modes of changing the heat flux and we used it earlier in [1]. We hence used harmonic analysis to process the results. Such a procedure for analyzing the measurement results yielded completely satisfactory results, although it was also relatively laborious. Later we noted that in conditions typical for many experiments the so-called regular mode of the second kind [6], the distinguishing peculiarity of which is the constant rate of change in the temperature of all points of the body, is successfully realized during heating and cooling cycles. The use of this peculiarity afforded the possibility of a new (and simpler) approach to the analysis of many experiments and the development of methods of processing the results, which are considerably more simple and convenient than the methods based on harmonic analysis. We shall examine this question in rather more detail below. Here we emphasize that the process of a

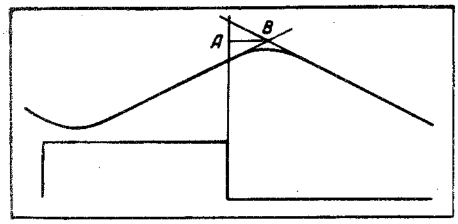

Fig. 1. Oscillogram of the temperature change.

periodic change in temperature (i.e., the so-called regular mode of the third kind [6]) is found to be quite abundant, and, in particular, can contain the regular mode of the second kind in itself and, as has been shown in [7], the regular mode of the first kind as well. We illustrate the effectiveness of the use of the process of periodic change in temperature by listing the fundamental methods, their modifications, and the apparatus produced at the University.

1. Methodology and apparatus to measure a complex of thermal properties based on the use of temperature waves being propagated along the axis of a cylindrical sample [1] (heating by electron bombardment). Used for the investigation of solid and liquid metals and semiconductors to a temperature of 1200°K.
2. Methodology to measure a complex of thermal properties of solid metals (several versions), based on the use of radial temperature waves produced in a cylindrical sample under modulated induction heating. Used for systematic investigations of the thermal properties of solid infusible metals, as well as for the electrical conductivity and radiativity in the 1000-2500°K temperature range [8, 9].
3. Methodology to measure a complex of thermal properties of metals (several versions), based on the use of radial temperature waves produced by electron bombardment. Used to study the properties of solid and principally liquid metals to a temperature of ~2000°K [1, 10, 11].
4. Apparatus to measure the heat conduction, specific heat, electrical conductivity and radiativities of thin metal samples (wire, foil) heated by a current. The method of periodic heating, used to measure the specific heat, is combined in the apparatus with the steady-state method of heat conductivity measurement [1, 12]. The temperature range is 1500-3000°K.
5. Methodology to measure a complex of thermal properties based on the use of a nonsteady-state method of heating metal samples by means of a current. The methodology has been developed at Moscow University [1] and has been realized in the laboratory of an electric-lamp equipment factory [13].
6. Methodology and apparatus to measure a complex of thermal properties of electrical conductive samples in the shape of disks, based on the use of periodically changing electron heating [14].
7. Methodology and apparatus (several versions) to measure a complex of thermal properties of mountain rocks, based on use of radial temperature waves [15, 16].
8. Methodology and apparatus to measure the temperature conductivity of mountain rocks and minerals, based on the use of the method of dense temperature waves with the application of periodic radiation heating [17, 18].
9. Methodology and apparatus to measure a complex of thermal properties of dielectrics, based on use of the method of temperature waves produced by a low-inertia electric heater placed between two identical samples [19].

There is sufficiently detailed information about the majority of the listed methods and apparatus in the literature. Here we consider only several more or less new methodological questions, namely, the development of the second of the described measurement methods, the sixth methodology in the presented list, and the new method mentioned above for the analysis and processing of the results for the Π-like modulation mode.

The methodology of measuring a complex of thermal characteristics using modulated heating by high-frequency currents is one of the most effective research methods. In this method, the sample under investigation is placed along the axis of the inductor of a high-frequency generator the power of which is changed periodically by means of a modulating circuit. Because heat liberation is at the surface during heating by high-frequency currents, the characteristics (amplitude and phase) of the radial temperature waves induced by the periodic heating of the surface layer prove to be substantially dependent on the thermal properties of the sample being studied. In the fundamental version of the method [8, 9] a solid cylindrical sample was used, the temperature fluctuations of its outer surface being recorded. Such a method of measurement, especially in conjunction with the contactless photoelectric method of recording the temperature fluctuations,

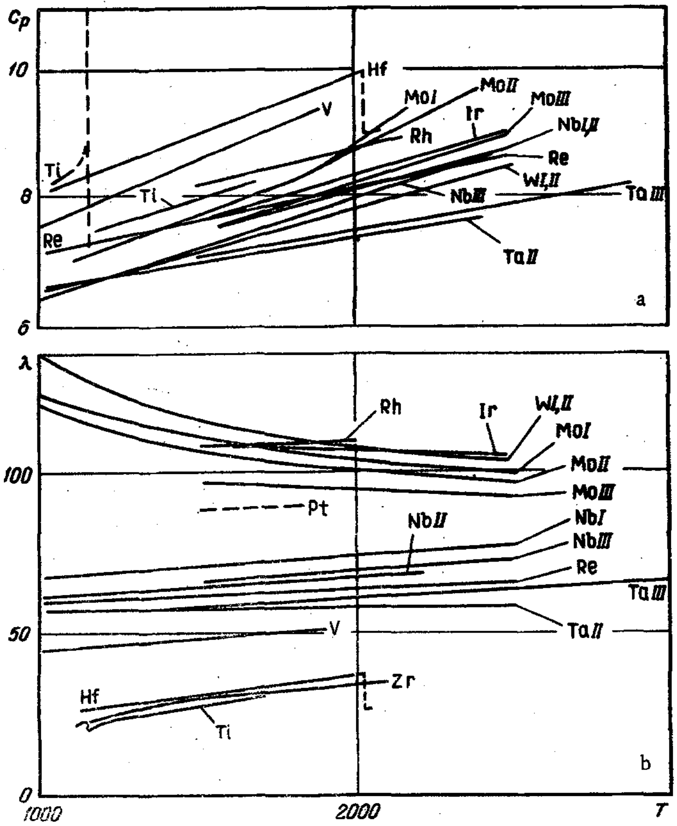

Fig. 2. Results of measuring the specific heat of metals (a), and the heat conductivity of metals (b). c_p, cal/g-atom·deg; λ, W/m·deg; T, °K.

is highly recommended and was used for systematic investigations of a complex of properties of solid infusible metals in a temperature range to 2500°K. The maximum error in measuring the temperature conduction, which consists of random and systematic errors, is hence $\sim$4%, and 5-7% for the specific heat and heat conduction. It has been shown in subsequent research by this method that the possibilities of alternating induction heating have been not at all exhausted by this. Aruntyunov [20] has developed and used a different version of the method, which differs from that described above in the use of a hollow cylindrical sample and the recording of the temperature fluctuations on its inner surface. It has hence been shown that such a scheme of measurement possesses significantly greater sensitivity to the sample characteristics being studied and consequently permits an improvement in the accuracy of the experiment. The systematic and random errors in determining the temperature conduction can be diminished almost twofold, while the errors in measuring the specific heat and the heat conductivity decrease by approximately 1%. A new version of the method with several modifications was subjected to detailed study and analysis in [20]. Measurements were performed on samples of diverse geometries, for different modulation frequencies; many parameters of the measuring circuit were varied, and data obtained for the diverse methods were compared. A new modification of the method was used to measure the properties of some infusible metals.

The second of the problems is the methodology and apparatus for measuring a complex of thermal properties of electrically conductive samples in the shape of disks, based on the use of the method of plane temperature waves. The crux of this method is the following. One of the surfaces of a disk sample of diameter 10 mm and thickness $\sim$1 mm is heated periodically by electron bombardment, while the temperature fluctuations on the side reverse to the heated surface are measured. The phase shift between the temperature fluctuations and the intensity of the electron heating is used to determine the temperature conductivity. Information as to the magnitude of the power periodically introduced to the sample, and the magnitude of the temperature fluctuations of the sample can be used to determine its specific heat. The fundamental peculiarities of the method and apparatus are the following. The electron current is modulated by a sinusoidal or square-wave law by using a control grid between the sample–anode and the heater–cathode (the grid voltage is supplied from a low-frequency generator). In substance, this construction is a power triode tube. The fluctuations in sample surface radiance are recorded by a photomultiplier, are magnified

TABLE 1. Sample Characteristics and Measurement Methods

Metals	Samples	Sample characteristics	Measurement method	Remarks
W	I	Rod. monocrystal $\varnothing = 8$, $l = 50$, 99,96 % (10^{-4} % Mo, $3\cdot10^{-2}$ % C)	Induction heating	[20]
	II	Rod, polycrystal $\varnothing = 13$, $l = 70$, 99,94 % ($3\cdot10^{-3}$ % Mo, $3\cdot10^{-2}$ % C)	The same	[20]
Mo	I	Rod, monocrystal $\varnothing = 10{,}4$, $l = 75$, 99,99 % ($5\cdot10^{-3}$ % C, $1\cdot10^{-3}$% O, $1\cdot10\ ^{3}$ Mg, $8\cdot10^{-4}$ % N, $4\cdot10^{-4}$ % Si, $9\cdot10^{-4}$ % H)	" "	[27], [32]
	II	Rod, monocrystal $\varnothing = 13{,}0$, $l = 75$, 99,9 % (0,01 % sequioxides ,10^{-2}% Ni)	" "	[27], [32]
	III	Wire $\phi = 0{,}05$, $\varnothing = 0{,}1$, $\varnothing = 0{,}2$, 99,98 % (0,003 % Mn, Fe, 0,002 % Cu, $5\cdot10^{-4}$ % Ni, $8\cdot10^{-4}$ Al, $9\cdot10^{-4}$ % Cr, $7\cdot10^{-4}$ % Pb)	Current heating	[12], [32]
V	I	Solid and hollow rod, polycrystal $\varnothing = 12$, $l = 90$, $\varnothing_{ou} = 3{,}6$, 4,8, 99,72 % (0,13 % Al, 0,09 % Si, 0,05 % Fe, 0,055 % O, 0,04 % C, 0,01 % Ni)	Induction heating	Two versions of the method were used [20], [27]
Nb	I	Rod, monocrystal $\varnothing = 13$, $l = 75$, 99,53 % (0,35 % Ta, 0,01 % C, 0,007 % Ni, 0,074 % W, 0,002 % Mo)	Induction heating	[27], [31]
	II	Rod, monocrystal 99,2 % (0,3 % Ta, 0,08 % Ti, 0,04 % Fe, 0,04 % Si)	Induction heating, heating by electron bombardment (radial temperature waves)	[27], [31]. See part of the results in [25]
	III	Wire $\varnothing$ 0,2, 99,62 % (0,28 % Ta, 0,05 % Fe, 0,015 % Mo with 0,01 % Ti, C)	Current heating	[12], [31]. Specifications are presented in [25] for the sample composition, while direct data are presented here

TABLE 1. (Continued)

Metals	Samples	Sample characteristics	Measurement method	Remarks
Ta	I	Rod, polycrystal ∅ = 12, $l = 98$, 99,8 % (0,13 % Nb, 0,008 % W, 0,005 % Mo with ~ 0,01 % Ti, Fe, Si, Al, C, O)	Induction heating	[20], [30]
	II	Rod, polycrystal ∅ = 7,3, $l = 66$, 99,6 % (0,33 % Nb, 0,02 % Mo, 0,014 % W)	Induction heating	[27], [30]
	III	Wire ∅ 0,2, 99,9 % (0,05 % Mo, 0,02 % Nb, with 0,01 % Ti, Si, Al)	Current heating	[12], [30]
Ir	I	Wire ∅ 0,2, 99,99 %	" "	[12], [29]
Rh	I	Wire ∅ 0,2, 99,99 %	" "	There is a misprint in [26]; the numbers on the figure should be shifted one division upward
Ti	I	Rod, polycrystal ∅ = 12, $l = 90$, 99,8 % (with 0,01 % Al, Cr, Ni, Mo, W, C, Si with 0,02 % Fe, N with 0,005 % Mn, Cu, 0,08 % O)	Induction heating	[20]
Zr	I	Rod, polycrystal ∅ = 9,2, $l = 66$, 99,44 % (0,2 % Al, 0,3 % Ti, 0,05 % Mg, 0,025 % Si, Mn)	The same	[20]
Hf	I	Rod, polycrystal 99,3 % (0,04 % SiO_2 with 0,003 % Fe_2O_3, Cr_2O_3, MgO, 0,004 % TiO_2, 0,001 % CaO, 0,006 % Al_2O_3, 0,65 % Zr)	" "	[20]
Re	I	Rod, monocrystal 99,99 % ($5 \cdot 10^{-3}$ O, $2 \cdot 10^{-4}$ Mo, $1 \cdot 10^{-4}$ Fe, Al, $5 \cdot 10^{-4}$ H, $4 \cdot 10^{-4}$ Si)	" "	[20], [8]. Data should be considered as preliminary since the measurement were conducted without taking account of anisotropy.

TABLE 2. Results of Measuring the Thermophysical Properties

Metals	Thermo-physical property	T, °K									T, °K											
		1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000
W I, II	a	(0,485)	0,463	0,443	0,424	0,407	0,391	0,376	0,363	0,352	0,341	0,332	0,324	0,315	0,307	0,298	(0,290)					
I, II	c_p	(6,47)	6,60	6,74	6,87	7,00	7,13	7,27	7,40	7,53	7,66	7,80	7,93	8,06	8,20	8,34	(8,47)					
I, II	λ	(136)	131,5	127	123	120	118	116	114	112	110,5	109	108	107	106	104,5	(104)					
I	ρ	(23,9)	27,1	30,3	33,5	36,7	39,8	43,0	46,2	49,5	52,8	56,2	59,6	63,0	66,5	69,9	73,4					
II	ρ	(24,3)	27,6	30,9	34,1	37,2	40,3	43,5	46,7	49,9	53,2	56,6	60,0	63,4	66,9	70,4	73,9					
, II	ε		0,120	0,139	0,154	0,169	0,182	0,194	0,205	0,216	0,226	0,234	0,242	0,250	0,256	0,260	0,265					
, II	ε_λ	(0,45$_8$)	0,45$_4$	0,45$_0$	0,44$_6$	0,44$_2$	0,43$_9$	0,43$_5$	0,43$_1$	0,42$_7$	0,42$_3$	0,41$_9$	0,41$_5$	0,42$_2$	0,40$_8$	0,40$_4$	0,40$_0$					
Mo , II	a	(0,415)	0,400	0,385	0,371	0,357	0,343	0,330	0,318	0,306	0,295	0,284	0,274	0,264	0,255	0,246	(0,237)					
I—III	c_p	(6,70)	6,85	7,00	7,15	7,29	7,45	7,62	7,80	8,02	8,25	8,48	8,74	9,00	9,25	9,50						
II I	c_p							7,62	7,80	7,96	8,12	8,28	8,48	8,61	8,78	8,95	9,00					
I	λ	(123,$_4$)	120,$_9$	118,$_4$	115,$_9$	113,$_5$	111,$_3$	109,$_5$	107,$_7$	106,$_4$	105,$_1$	103,$_3$	102,$_9$	102,$_1$	101,$_3$	100,$_5$	(99,$_7$					
II	λ	(120)	117,$_4$	114,$_9$	112,$_4$	110,$_1$	108,$_1$	106,$_3$	104,$_6$	103,$_3$	102,$_1$	101,$_0$	100,$_0$	99,$_2$	98,$_4$	97,$_7$	(97)					
III	λ						97,5	97	96,5	96	95,5	95	94,5	94	93,5	93	92,5					
I	ρ	(23)	26,0	28,9	31,8	34,7	37,6	40,5	43,4	46,5	49,6	52,8	56,0	59,2	62,6	65,8	(69,$_2$)					
II	ρ	(24,$_5$)	27,5	30,6	33,6	36,6	39,6	42,7	45,7	48,9	52,5	55,5	58,8	62,1	65,4	68,7	(72)					
III	ρ						38,4	41,6	44,8	48,0	51,2	54,4	57,6	60,7	64,8	66,7	69,6					
I, II	ε	(0,087)	0,098	0,109	0,120	0,131	0,142	0,152	0,161	0,171	0,180	0,189	0,198	0,206	0,213	0,221	(0,228)					
III	ε						0,165	0,175	0,185	0,195	0,205	0,215	0,225	0,235	0,245	0,255	0,265					
I—III	ε_λ	(0,420)	0,415	0,41	0,405	0,40	0,395	0,39	0,385	0,38	0,375	0,37	0,365	0,36	0,355	0,35	(0,345)					
V	a	0,123$_2$	0,122$_6$	0,121$_9$	0,121$_3$	0,120$_7$	0,120$_0$	0,119$_3$	0,118$_7$	0,118$_1$	0,117$_5$											
	c_p	7,56	7,77	7,97	8,18	8,38	8,59	8,79	9,00	9,20	9,41											
	λ	45,$_0$	45,$_8$	46,$_6$	47,$_3$	48,$_0$	48,$_6$	49,$_2$	49,$_8$	50,$_4$	51,$_0$											
	ρ	68,0	73,4	78,5	83,5	88,2	92,8	97,5	101,5	105,6	109,5											
	ε	0,157	0,173	0,186	0,198	0,207	0,215	0,221	0,226	0,230	0,233											
	ε_λ			0,42$_2$	0,41$_8$	0,41$_3$	0,40$_8$	0,40$_3$	0,39$_9$	0,39$_4$	0,38$_9$											
Nb I	a	(0,272)	0,270	0,268	0,266	0,263	0,261	0,259	0,257	0,254	0,252	0,250	0,248	0,246	0,243	0,241	(0,239)					
II	a	(0,252)	0,250	0,248	0,246	0,244	0,241	0,239	0,237	0,235	0,233	0,231	0,228	0,226								
I, II	c_p	(6,40)	6,56	6,72	6,88	7,04	7,20	7,36	7,52	7,68	7,84	8,00	8,17	8,33	8,49	8,65	(8,81)					
III	c_p						7,44	7,56	7,68	7,80	7,93	8,06	8,20	8,33	8,44	8,60	(8,73)					
I	λ	(67,2)	67,9	68,6	69,2	69,9	70,6	71,3	71,9	72,6	73,3	74,0	74,7	75,4	76,0	76,7	(77,3)					
II	λ	(61,6)	62,2	62,8	63,4	64,0	64,6	65,3	65,9	66,5	67,1	67,7	68,4	69,0								
III	λ						66,0	66,7	67,3	68,0	68,7	69,3	70,0	70,7	71,3	72,0	(72,7)					
I	ρ	(42,5)	45,6	48,7	51,8	54,9	58,0	60,9	63,8	66,6	69,6	72,4	75,3	78,4	81,3	84,3	(87,4)					
II	ρ	(45,8)	48,3	51,8	55,1	58,3	61,2	64,0	66,8	69,6	72,4	75,2	78,0	80,7								
III	ρ			47,7	50,9	54,1	57,3	60,5	63,6	66,7	69,9	73,0	76,2	79,4	82,6	85,8	(89)					
I, II	ε	(0,108)	0,118	0,128	0,137	0,147	0,156	0,165	0,174	0,188	0,192	0,200	0,208	0,216	0,224	0,231	(0,238)					
III	ε				0,17	0,18	0,19	0,20	0,205	0,215	0,225	0,235	0,245	0,255	0,265	0,27	0,27					
I—III	ε_λ				0,38$_4$	0,38$_1$	0,37$_8$	0,37$_5$	0,37$_2$	0,36$_9$	0,36$_6$	0,36$_4$	0,36$_1$	0,35$_8$	0,35$_5$	0,35$_2$	(0,34$_9$)					
Ir	c_p						7,59	7,73	7,88	8,03	8,17	8,32	8,47	8,61	8,76	8,90	9,05					
	λ						109	109	108,5	108	108	107,5	107	107	106,5	106	(105)					
	ρ						34,4	37,3	40,2	43,5	46,4	49,2	51,9	54,6	57,4	60,2	63,0					
	ε				0,129	0,136	0,143	0,149	0,156	0,163	0,170	0,177	0,183	0,190	0,197	0,204	0,211					
	ε_λ				0,272	0,267	0,262	0,257	0,253	0,248	0,243	0,238	0,233	0,229	0,224	0,219	0,215					
Rh	c_p						8,18	8,30	8,41	8,52	8,64	8,76	8,88	(9,00)								
	λ						108	108	109	109	110	110	(111)									
	ρ				28,1	30,9	33,8	36,6	39,5	41,6	44,9	47,5	(50)									
	ε				0,13	0,135	0,14	0,145	0,15	0,155	0,16	0,165	0,17	(0,175)								
	ε_λ				0,26	0,25	0,24	0,23$_5$	0,23	0,22$_5$	0,21$_5$	0,20$_5$	0,20									
Ti	a	(0,068)	0,069	0,081	0,085	0,088	0,091	0,094$_5$	0,098													
	c_p	(8,20)	8,40	7,52	7,67	7,82	7,97	8,12	8,27													
	λ	(21,0)	22,0	23,5	25,0	26,3	27,7	29,2	30,7													
	ρ	155	162	150,5	152,8	154,8	156,9	159,0	161,0													
	ε	0,246	0,254	0,247	0,252	0,257	0,262	0,267	0,272													

TABLE 2. (Continued).

Metals	Thermo-physical property	T, °K																				
		1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	30 0
	ε_λ		(0,50)	0,483	0,480	0,476	0,473	0,470	0,467													
Zr	a		0,096	0,105	0,135	0,142	0,144	0,146	0,148	0,150	0,151	0,152	0,153									
	c_p		8,82	8,46	7,80	7,80	8,00	8,11	8,25	8,42	8,60	8,74	8,90									
	λ		21,6	23,5	26,8	29,1	30,0	30,8	31,5	32,3	33,0	33,6	34,4									
	ρ		135,8	116,5	118,0	120,0	121,9	124,0	126,2	128,3	130,4	132,4	134,5									
	ε		0,240	0,226	0,227	0,232	0,238	0,244	0,925	0,256	0,262	0,268	0,274									
	ε_λ		0,48	0,47	0,455	0,445	0,435	0,425	0,42	0,41	0,405	0,40										
Hf	a	(0,093)	0,096	0,099	0,102	0,105	0,109	0,112	0,115	0,118	0,122	0,122	0,093									
	c_p	(8,05)	8,25	8,42	8,60	8,78	8,98	9,17	9,35	9,52	9,70	9,90	$9,0_5$									
	λ	(24)	25,6	27,0	28,4	29,5	30,6	31,9	33,2	34,4	35,6	36,7	27									
	ρ		137,0	146,5	153,0	154,1	160,8	163	164,6	165,0	165,6	164,9	155,4	(157,5)								
	ε	(0,26)	0,266	0,272	0,284	0,291	0,299	0,306	0,312	0,318	0,324	0,322	0,307	(0,32)								
	ε_λ				0,465	$0,45_5$	$0,45_5$	$0,45_5$	$0,45_5$	$0,45_5$	$0,45_5$											
Re	a	(0,181)	0,181	0,180	0,180	0,179	0,179	0,178	0,177	0,176	0,175	0,175	0,174	0,174	0,173	0,172	0,171					
	c_p	(7,12)	7,22	7,32	7,42	7,52	7,62	7,72	7,82	7,92	8,02	8,13	8,23	8,33	8,43	8,54	8,64					
	λ	(59,5)	60,1	60,6	61,1	61,5	61,9	62,3	62,7	63,1	63,5	63,9	64,3	64,6	65,0	65,3	65,6					
	ρ	(65,5)	69,5	73,8	77,2	80,9	83,6	87,2	90,7	93,4	96,2	98,9	101,0	103,0	105,1	106,9	108,8					
	ε	(0,16)	0,17	0,18	0,189	0,198	0,206	0,24	0,222	0,230	0,238	0,246	0,253	0,260	0,268	0,275	9,282	0				
	ε_λ	(0,44)	$0,43_5$	0,43	$0,42_5$	0,42	$0,41_5$	0,41	$0,40_5$	0,40	$0,39_5$	0,39	$0,38_5$	0,38	$0,37_5$	0,37	$0,36_5$					
Ta I	a	(0,237)	0,236	0,235	0,233	0,232	0,230	0,229	0,228	0,227	0,225	0,223	0,221	0,220	0,219	(0,217)						
II	a	(0,229)	0,227	0,225	0,223	0,222	0,220	0,218	0,216	0,215	0,213	0,211	0,209	0,208	0,206	0,204	(0,202)					
I	c_p	(6,67)	6,75	6,83	6,92	7,00	7,05	7,10	7,15	7,20	7,25	7,30	7,37	7,43	7,50	(7,57)						
II	c_p	(6,59)	6,67	6,75	6,82	6,90	6,48	7,06	7,14	7,22	7,30	7,37	7,45	7,53	7,60	7,68	(7,76)					
III	c_p						7,05	7,13	7,23	7,31	7,39	7 49	7,57	7,66	7,75	7,83	7,92	8,01	8,09	8,17	8,25	
I	λ	(59,3)	59,6	59,9	60,2	60,5	60,8	61,1	61,4	61,7	62,0	62,3	62,6	62,9	63,2	(63,5)						
II	λ	(56,8)	56,9	57,0	57,1	57,2	57,3	57,4	57,5	57,6	57,7	57,8	57,8	57,9	58,0	58,1	(58,2)					
III	λ					57,5	58,0	58,5	59,0	59,5	60,5	61,0	61,5	62	62,5	63,0	64,0	64,5	65	65,6	66,3	(67)
I	ρ	(43,0)	46,9	50,9	55,6	58,3	61,7	65,1	68,5	71,8	75,0	78,5	81,8	85,0	88,4	(91,7)						
II	ρ	(45,6)	49,6	53,6	57,3	60,9	64,4	67,8	71,2	74,4	77,6	81,0	84,4	87,6	91,0	94,3	97,7					
III	ρ				55,5	59,5	63,0	66,8	70,2	73,4	76,6	80,0	83,3	86,4	89,4	92,4	95,4	98,5	101,5	104,5	107,5	(111)
I	ε		0,123	0,137	0,152	0,159	0,167	0,174	0,181	0,189	0,196	0,203	0,210	0,219	0,225	0,233	(0,24)					
II	ε	(0,13)	0,140	0,149	0,159	0,168	0,178	0,187	0,196	0,204	0,213	0,221	0,230	0,238	0,246	0,254	0,263					
III	ε				0,16	0,17	0,18	0,19	0,20	0,21	0,22	0,23	0,24	0,25	0,26	0,27	0,28	0,29	0,30	0,31	0,32	(0,33)
I—III	ε_λ			(0,47)	$0,44_9$	$0,44_1$	$0,43_5$	$0,43_1$	$0,42_7$	$0,42_4$	$0,42_1$	$0,41_8$	0,416	$0,41_4$	$0,41_2$	$0,41_0$	$0,40_8$	$0,40_6$	0,40	$0,40_2$	0,40	(0,40)

Note. a, cm²/sec; c_p, kcal/g-atom·deg; λ, W/m·deg; ρ, μΩ·cm. Figures in parentheses were obtained by extrapolation (in the limits of 100°).

by a low-frequency amplifier, and are recorded on a loop oscilloscope the other channel of which records the change in plate current.

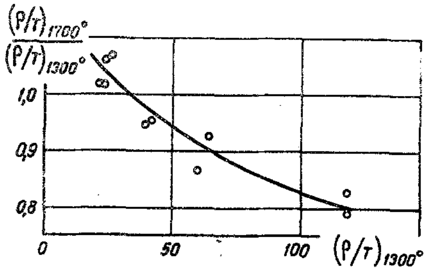

Fig. 3. Dependence of $(\rho/T)_{T=1300°K}/(\rho/T)_{T=1700°K}$ on $(\rho/T)_{T=1300°K}$.

The ultimately simple geometry of the sample and its small size make this method convenient for the investigation of materials that are hard to process and difficultly available. Because the method admits of exclusion of the influence of heat exchange (see [16, 18]), the sample thickness is not constrained, i.e., the method is also applicable for comparatively thick samples (for porous and coarse-grained materials). The error in measuring the temperature conductivity is due mainly to the error in measuring the phase shift. This error is usually 0.5° in practice. For optimal values of the heating frequency its influence on the measurement of the temperature conductivity is ~2.5%. Taking account of the error because of inaccurate insertion of corrections to the heat exchange and the inertia of the recording apparatus, we hence add a ~2% error, and the total error in measuring the temperature conductivity is hence not more than 5%. The maximum error in measuring the specific heat is 4% (mainly because of errors in determining the power and amplitude of the temperature fluctuations).

Besides measuring the thermal characteristics, the electrical resistivity of the very same sample was measured with this equipment by the method proposed in [21]. The essence of the method is that a dc current is supplied to two adjacent pins out of four which are disposed mutually perpendicularly in the plane of the sample, and the voltage is taken from the other two by a compensation method. The electrical resistivity of the sample is found by means of the known voltage drop on one of the sample sections and the current on the adjacent section. The error in measuring the electrical resistivity by this method is ~2%.

Let us note that there exists the possibility of measuring the degree of blackness (emissivity) of the sample under investigation on this apparatus.

The operation of the apparatus was studied by investigating the thermal properties and electrical conductivity of molybdenum and niobium. The experiment was accomplished under diverse condtions (the heating frequency, sample thickness and diameter, etc., were widely varied). Consistency of the data is obtained. There is also satisfactory correspondence between the data obtained and those in the literature.

At present research is continuing to perfect and develop further this method of measurement.

The last of the new methodological questions which we shall discuss here is the new method mentioned already above, of analyzing and processing the results for Π-like modulation. This method has been studied in detail and tried out in application to the method of radial temperature waves produced by heating the inner surface of a hollow cylindrical sample using electron bombardment. The method is based on the existence of a rectilinear section on the experimentally recorded curve of temperature variation (see Fig. 1). We have showed in [22] that the specific heat can be determined by the slope of these sections and the known heating intensity, with an error not exceeding the error in processing the same curves using harmonic analysis. A method of using the same curve sections to determine the temperature conductivity has been proposed in [23]. It can be shown by sufficiently simple computations that the magnitude of the temperature conductivity is inversely proportional to the spacing between the intersection of the asymptotes of the linear sections and the time of the change in the heating intensity (the section AB in Fig. 1). This method of processing the results was checked thoroughly in [24]. Data obtained using diverse processing methods under diverse conditions, were compared; computational formulas were found to take account of corrections when using a composite cylinder (to take account of the crucible walls when working with liquid metals), and the conditions of applicability of the new method were analyzed. It was hence clarified that the new processing method is no less accurate than the method of harmonic analysis and yields an approximately tenfold saving in the time expended in processing. In addition to its principal advantage, this method has has another, in that it permits extension of the range of modulating frequencies towards higher periods and, consequently, increases the possibility of its utilization. It is indubitably expedient to extend the new processing method also to other periodic heating methods.

Let us turn to a discussion of the measurement results.

Let us first examine results from studying the properties of infusible metals.

The characteristics of the studied samples are presented in Table 1 and the list of data in Table 2.

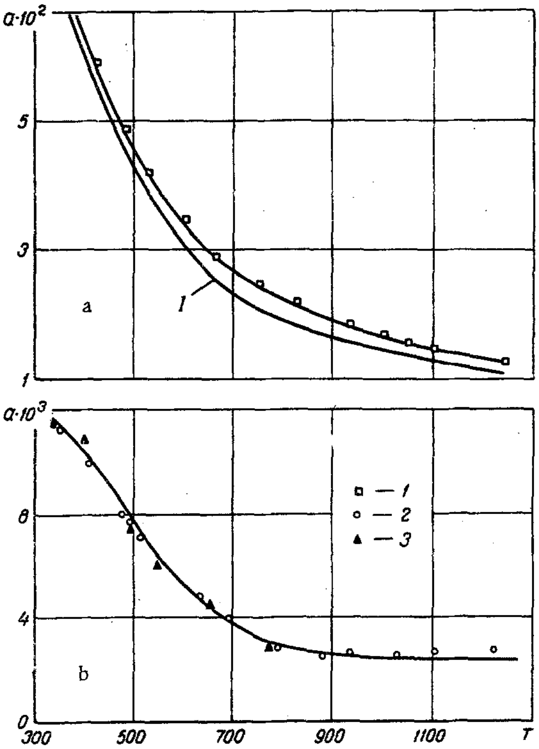

Fig. 4. Dependence of the temperature conductivity, cm^2/sec, of aluminum oxide (a) and granite (b) on the temperature, °K: 1, 2) data obtained on apparatus No. 8; 3) on apparatus No. 9; I) on apparatus No. 7.

The reliability of the experimental material obtained was checked repeatedly by variation in the fundamental experimental conditions (the sample size, the frequency and amplitude of the temperature fluctuations) and by comparison of the data obtained in diverse versions of the methods. Data for the specific heat are presented in Fig. 2a.

In the analysis of the experimental material obtained, there was a striking absence of a rise in the specific heat of molybdenum, tantalum, niobium, vanadium, iridium, and rhodium in the temperature range above 0.8 T_m, which was observed for the first three metals in the researches of Ya. A. Kraftmakher and some others, and was associated with the role of thermal vacancies (see [33]). The data obtained oblige us again to pose the question of the role of the vacancies. This question merits a separate discussion.

The second conclusion relating to the temperature dependence of the specific heat c_p is the closeness of the functions $c_p(T/T_m)$ (T_m is the melting point) for different metals. The deviations of the measurement results from the general line

$$c_p = 6 + 3\frac{T}{T_m}, \tag{1}$$

do not exceed 5% as a rule. It should be noted that extrapolation of the dependence for c_p to $T = 0$ yields a value of 6 cal/g-atom · deg in conformity with the Dulong and Petit law.

The question of the behavior of the specific heat for constant volume is related to the role of anharmony of the lattice vibrations and the contribution of electron specific heat. There are researches in which data obtained at low temperatures are used to eliminate the latter of these factors (see [34-47], for example).

Application of such a scheme to the material that we obtained yields a picture for the anharmonic contribution which cannot be called uniform. A large negative contribution is obtained for vanadium, tantalum, and niobium, and a positive contribution for molybdenum and tungsten which possess the same body-centered cubic lattice; an anharmonic contribution obtained for iridium and rhodium is negligible.

Although theory does not, in principle, exclude a different sign for the anharmonic contribution, it is difficult to reconcile such results with the similarity observed in the other properties of the metals under consideration (the closeness of the ratio between the heat of fusion per gram atom and the absolute melting point, the ratio of the heat of evaporation to the heat of fusion, the product of the expansion coefficient and the absolute melting point, the Grunhausen parameters) and finally, with the existence of uniformity in the temperature dependence of c_p.

A more probable explanation of such a situation is the difference between the coefficient of electron specific heat γ at high temperatures and its low-temperature value. From the viewpoint of the electron theory of metals this can be the result, say, of electron–phonon interaction which influences the electron energy distribution at low temperatures and is inessential at high temperatures. Theoretical estimates of this effect, presented in [38] for tantalum and tungsten and in [39] for vanadium, are in good agreement with the experimental data obtained. Thus, for vanadium $\gamma_0/\gamma = 1.9$ according to Krebs, while we find $\gamma_0/\gamma \sim 1.7$.

Further research in the region of investigating the specific heat of solid infusible metals is associated with the refinement of the $c_p - c_v$ values, for which it is extremely desirable to formulate experiments devoted to a study of compressibility in the high temperature range by means of ultraacoustic techniques.

Let us turn to an analysis of the results on the heat conductivity of solid infusible metals.

The results are presented in Fig. 2b and in Table 2, together with the results of measuring the electrical conductivity. It can be seen that in just two cases (for tungsten and molybdenum) is the picture predicted by elementary electron theory observed – the decrease in heat conductivity with temperature and the tendency to an asymptotic value. In all the other cases the heat conductivity either increases with temperature or is practically independent of the temperature.

An analysis of the factors governing the behavior of the heat conductivity results in a more-or-less natural deduction that the temperature dependence of the heat conductivity λ is determined primarily by the nature of the temperature dependence of the electrical conductivity, by the deviation from a linear temperature dependence of the resistivity ρ. There is a slight increase in the quantity ρ/T with temperature for tungsten and molybdenum, and a decrease for the majority of the other metals. The stronger the decrease in ρ/T with temperature, the steeper the temperature dependence $\lambda(T)$.

An analysis of the experimental curves $\rho/T = f(T)$ reveals a regularity that is interesting, in our opinion: the greater the specific resistivity, the steeper the drop in ρ/T as the temperature increases. In other words, the relative change in ρ/T with temperature correlates with the absolute value of ρ/T. This is illustrated in Fig. 3, where values of ρ/T are plotted along the horizontal axis for a 1300°K temperature, and the ratio of ρ/T at 1300°K to ρ/T at 1700°K is plotted along the vertical axis. The correlation under consideration can be associated with the Mott reasoning about the electrical conductivity of the transition metals. The greater the role of the s–d interaction in the absolute values of the specific resistivity, the greater will be its influence on the temperature coefficient.

Analysis of the behavior of the Lorentz numbers of the metals studied results in a deduction about the relatively small role of lattice heat conductivity. The fraction of the lattice heat conductivity exceeds 30% only in tungsten. Extraction of the magnitude of the lattice component in the traditional manner, using the Lorentz number calculated by Sommerfeld for the electron component, results in the deduction that the lattice heat conductivity is of the same order as for infusible oxides. As regards the more exact details, the existence of a correlation between λ_{lattice}, on the one hand, and the product of the speed of sound in a metal and the melting point, on the other hand, is here successfully established. This regularity can be explained by using similarity theory and an elementary model of heat transport by the lattice.

Let us now turn to the results of investigating the properties of nonmetallic materials.

To illustrate the operation of the apparatus and the nature of the behavior of the thermal properties of dielectrics, the temperature conductivity of a typical mineral, polycrystalline aluminum oxide, and a typical mountain rock, granite, as a function of the temperature is presented in Fig. 4a, b. The temperature conductivity of the aluminum oxide (density 3.94 g/cm^3) was measured on apparatuses Nos. 7 and 8 for the same sample. Some systematic discrepancies between the data obtained by different means can be associated with the inaccuracy in determining the position of the thermocouples in the sample in an apparatus based on the method of radial temperature waves. Good agreement is also observed in the data for granite (medium granularity, density 2.63 g/cm^3, porosity 2.6%) obtained on apparatuses Nos. 8 and 9 (see Fig. 4b). The nature of the temperature change in the temperature conductivity of these samples is typical for dielectrics in the 300-1300°K temperature range. The diminution in the temperature conductivity as the temperature rises corresponds entirely with the standard ideas about the transport of heat in crystalline objects at high temperatures: the scattering of heat by oscillations of the lattice atoms. It should be noted that the absolute value of the temperature conductivity of a pure mineral is an order of magnitude greater than the corresponding value for mountain rock.

The properties of a number of mountain rocks and minerals were measured on apparatuses Nos. 7, 8, and 9. Thus, all the thermal characteristics of fourteen samples of periodite and peroxenite were measured to temperatures of ~1300°K on apparatus No. 7, and the temperature conductivity of thirteen samples of basalt, granite, diorite, gabbro, and some minerals (feldspar, plagioclase) to a temperature of 1300°K on apparatus No. 8. All the thermal properties of the same samples as had been measured on apparatus No. 8 were measured on apparatus No. 9 to a temperature of 800°K. The chemical composition, petrographic analysis, porosity and density before and after heating, and occurrence are known for all the measured samples.

The aim of the research presently being conducted is to make effective use of the experimental material obtained in solving fundamental geothermal problems.

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