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Change in the normal spectral emissivity during melting of elements

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An experimental and computational study of the normal spectral emissivity during melting of various metals was carried out, the installation scheme and the method of conducting experiments were given. The possibilities of the electromagnetic theory for describing the dependence of the behavior of the normal spectral emissivity of metals and semimetals are evaluated.

Keywords: normal spectral emissivity, wavelength, metal, electromagnetic theory.

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Introduction

The scientific literature has a limited number of the experimental data on the normal spectral degrees of emissivity of liquid and solid pure substances. Knowledge of these parameters is required for quantitative and qualitative analyses of the heat exchange in heavy-duty heat-exchanging equipment. This is why the relevance of this scientific problem remains quite high.

Today, the publications of different authors [1–5] deal with both the procedure of spectral measurements of normal emissivity of pure metals, and the experimental data themselves within a wide temperature range, including solid-to-liquid phase transformation.

Earlier it was considered (see the studies [6,7]) that monochromatic degrees of emissivity of metals close to visible range of spectrum are not changed at the solid-to-liquid transformation.

The authors of the study [8] mentioned based on the measurements of spectral degrees of emissivity that with the wavelength $0.65\,\mu$m of liquid hard-melting metals — molybdenum, niobium, vanadium and titanium — it is impossible to definitely conclude on changes in the monochromatic emissivity during melting or whether it changes at all.

The author of the monograph [9] concludes that close to the melting point of different metals within the range of wavelengths 0.4 to $2\,\mu$m there is no stepped change in normal spectral emissivity. Numerical growth of the degrees of liquid metal emissivity versus that of solid state is comparable to change of specific electrical resistance at the same temperature values. Another monograph by the same author [10] recommends spectral degrees of emissivity of 24 metals calculated by using the Hagen–Rubens relation [9], which does not include arbitrary constants and allows to determine the spectral emissivity as the function of conductivity.

The recent studies in this field [11–13] show change by the decrease of normal spectral emissivity of a series of metals (titanium, vanadium, molybdenum) from the wavelength and coherence with the semi-empirical estimate based on the Drude model [14].

The purpose of this study is to experimentally find normal spectral emissivity of a series of metals in the field of melting temperatures in solid and liquid states, including the analysis of the obtained results.

1. Experiment description

The authors hereof performed the study of normal spectral emissivity of lead, tin, zinc, cadmium, bismuth and antimony on the experimental bench (Fig. 1) with modified accessories of the internal space of a measuring cell. Unlike the cell presented in [15], they used radiometer with built-in replaceable narrow-band filter. The narrow-band infrared disperse filters are made by the Central Design Bureau with experimental manufacturing site of the Institute of Physics of the Academy of Sciences of the Republic of Belarus (Table 1).

The study performed the measurement of ratio of normal spectral degrees of emissivity of melted and polished metal (semi-metal) at the temperature of the experiment, including the melting point: $\varphi_\lambda = \varepsilon_{\lambda,liquid}/\varepsilon_{\lambda,solid}$, where $\varepsilon_{\lambda,liquid}$, $\varepsilon_{\lambda,solid}$ — is the normal spectral degree of emissivity of metal (semi-metal) in liquid and solid phases, accordingly.

The studies were performed at the wavelengths (λ) from 0.69 to $10.6\,\mu$m. The selected range of the wavelengths is beyond the red limit of photo effect, therefore, it cannot have impact to the obtained results of the experiment. The filter in each experimental measurement

Table 1. Spectral characteristics of the narrow-band filters

Filter No.	1	2	3	4	5	6
Bandpass of the filter, μm	0.69	1.63	1.97	4.2	7.3	10.6

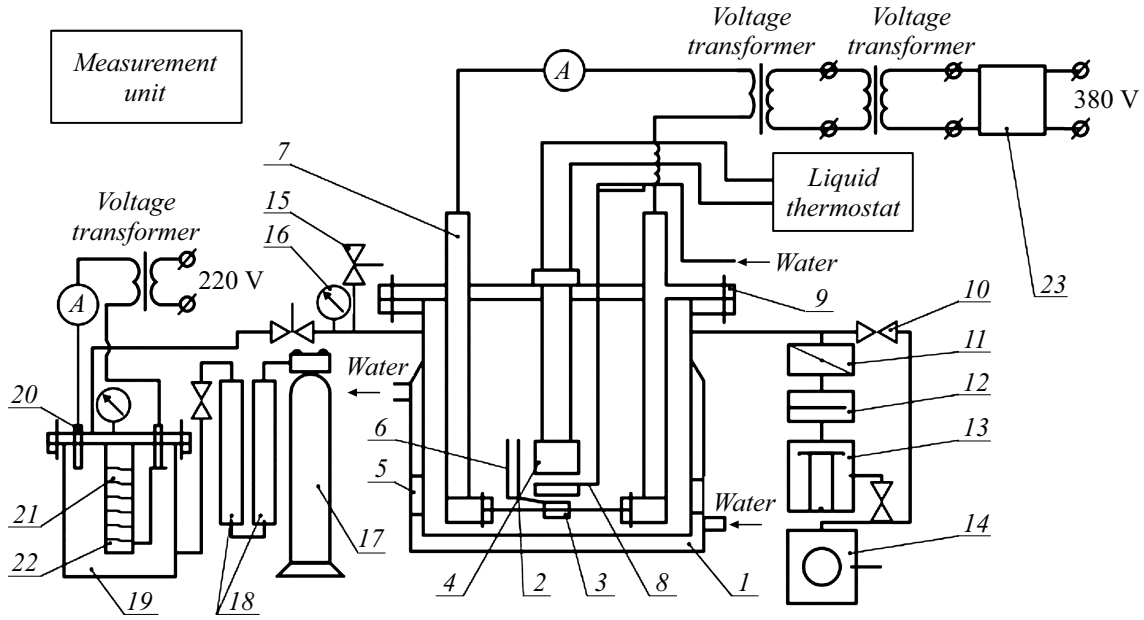

Figure 1. Diagram of the experimental bench: *1* — housing, *2* — heating belt, *3* — metal under study, *4* — radiometer with built-in narrow-band replaceable filter, *5* — window, *6* — thermocouples, *7* — cooled current input leads, *8* — water-cooled shutter, *9* — cover, *10* — valves, *11* — gate, *12* — trap, *13* — diffusion pump, *14* — backing vacuum pump, *15* — inlet valves system, *16* — vacuum gage, *17* — inert gas (argon) vessel, *18* — mechanical filters, *19* — gas treatment capacity, *20* — water-cooled current input leads, *21* — porcelain pipe, *22* — tungsten spiral, *23* — voltage stabilizers.

was set in the radiometer between the thermal element and temperature-controlled diaphragms.

The experimental studies used the absolute radiation method. The vacuum in the experimental bench was reaching 10^{-2} Pa, and further it was filled with special dried and softened inert gas (argon) up to the pressure of 10^5 Pa. Thermostat maintained constant temperature of the radiometer with the narrow-band filter equal to 293 ± 0.1 K. Cooling liquid (distillated water) was fed both into jacket of working chamber and into the hollow spaces of current input leads, to which the model of absolute black body or resistive heater belt was secured together with a substance under study. All experimental measurements were performed upon reaching the steady-state mode. Zero value of the thermal EMF of the emission detector meant its proper temperature control function and availability for the work. Radiometer with built-in narrow-band filter graduated by the detachable cylindrical model of the absolute black body (ABB) upon reaching the equality of the temperatures of the model „bottom“ and the walls.

The maximum temperatures of metals in the experiments were limited to the liquid metal evaporation rate or its boiling point. The state of metallic mirror surface was controlled visually during the whole experiment. The melt surface was considered as optically smooth. During crystallization the surface, as a rule, had got rough with a recess in the form of a crater in the center. Such spectral degree of emissivity of the sample with the surface like that appeared to be elevated. This is why the surface of hardened sample removed from the heater was ground and polished up to aspect of a mirror, including the metal surface quality assessment by means of profilometer.

According to the existing procedure of GOST R 8.736-2011, the authors performed assessment of the experiment error, that included systematical and accidental errors. The maximum relative error was $\pm 2\%$. Subject to graduation of the applied reference thermocouple made of platina-rhodium, the maximum error of the experiment was assessed 5 to 8%, depending on the temperature.

2. Research results

The obtained experimental values of the ratio φ_λ — normal spectral emissivity of liquid metals versus the same in solid state close to the melting points — are given in Table 2.

For the studied metals in the field $0.69\,\mu$m of spectrum φ_λ is close to one (Fig. 2), i.e. metal or semi-metal emit similarly, no phase transformation impact was registered. This result is coherent to the existing measurements within the visible range of spectrum (from 0.4 to $0.7\,\mu$m) [9,10]. As far the wavelength is growing, it was registered that the value φ_λ starts deviating from one, with quite abrupt spike for metals and fall for semi-metals.

The highest changes of values φ_λ are observed for zinc (2.4 times) and cadmium (1.95 times). The same metals during melting have the highest increase in the integral normal hemispheric degree of emissivity.

Table 2. Experimental values

Transmission band, μm	Ratio of normal spectral emissivity$\varphi_{\lambda n\epsilon}$ $T_{melting}$, K					
	Lead 600	Tin 505	Zinc 693	Cadmium 594	Bismuth 544	Antimony 903
0.69	1.02	1.03	1.02	1.01	0.99	0.99
1.63	1.03	1.04	1.07	1.03	0.99	0.99
1.97	1.04	1.05	1.12	1.07	0.98	0.97
4.2	1.10	1.06	1.26	1.15	0.97	0.96
7.3	1.44	1.38	1.93	1.57	0.94	0.92
10.6	1.64	1.48	2.39	1.95	0.87	0.81

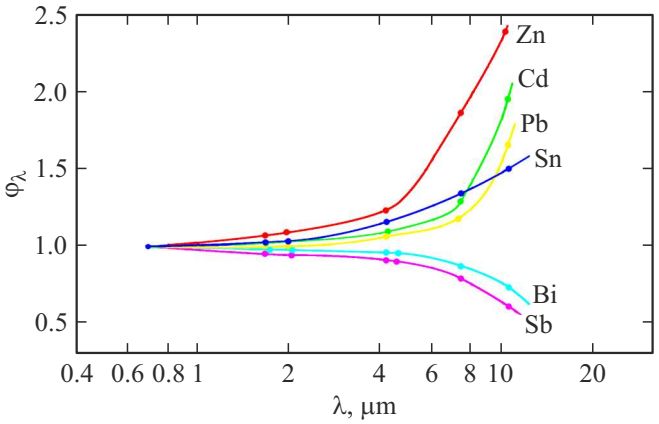

Figure 2. Value φ_λ for zinc, cadmium, tin, lead, antimony and bismuth — field of the elements melting.

3. Theoretical approaches

Consider the applicability of electromagnetic theory for analysis of change of the spectral degree of emissivity when melting six studied elements.

In accordance with the Drude formula, having considered it is true for liquid phase as well, there are

$$\varphi_{\lambda 1} = \frac{\varepsilon_{\lambda,liquid}}{\varepsilon_{\lambda,solid}} = \sqrt{\frac{\rho_{liquid}}{\rho_{solid}}}, \tag{1}$$

$$\varphi_{\lambda 2} = \frac{\varepsilon_{\lambda,liquid}}{\varepsilon_{\lambda,solid}} = \sqrt{\frac{\rho_{liquid}}{\rho_{solid}}} \times \frac{1 - 0.188\sqrt{\rho_{liquid}/\lambda} + 0.0249\rho_{liquid}/\lambda}{1 - 0.188\sqrt{\rho_{solid}/\lambda} + 0.0249\rho_{solid}/\lambda}, \tag{2}$$

$$\varphi_{\lambda 3} = \frac{\varepsilon_{\lambda,liquid}}{\varepsilon_{\lambda,solid}} = \sqrt{\frac{\rho_{liquid}}{\rho_{solid}}} \times \frac{1 - 0.184\sqrt{\rho_{liquid}/\lambda} + 0.0329\rho_{liquid}/\lambda - 2\pi c\tau \times (0.5/\lambda - 0.184\sqrt{\rho_{liquid}/\lambda^{1.5}} + 0.049\rho_{liquid}/\lambda^2)}{1 - 0.184\sqrt{\rho_{solid}/\lambda} + 0.0329\rho_{solid}/\lambda - 2\pi c\tau \times (0.5/\lambda - 0.184\sqrt{\rho_{solid}/\lambda^{1.5}} + 0.049\rho_{solid}/\lambda^2)}, \tag{3}$$

where $\rho_{solid}, \rho_{liquid}$ — specific electrical conductivity of metal at the experiment temperature in solid and liquid phases, accordingly; c — light speed; τ — electron relaxation time; $\varphi_{\lambda 1}, \varphi_{\lambda 2}, \varphi_{\lambda 3}$ — ratio of normal spectral emissivity of liquid metals to that in solid state close to melting points, calculated based on [14,16,17], accordingly.

Specific electrical conductivity of metals and semi-metals has a high dependence on the temperature [18,19]. At the temperatures of phase transformation there is a spike change of the parameter ρ. Thus, e.g., in liquid tin [20] close the melting point 793 K there is a stepped change of the thermal EMF and break of the dependence of electrical conductivity on the temperature (Fig. 3).

The ratio (1) results in a spike of the degree of emissivity independent on the wavelength. The same values of spike occur according to the Drude formula and for the integral degree of emissivity. Two more ratios (2) and (3) include the first multiplier equal to the expression (1). The second multiplier in them refers to fractions, whose numerical values are close to one.

Figures 4–7 show changes of normal spectral degrees of emissivity depending on the wavelength and spikes of integral degrees of emissivity during melting of zinc, cadmium, tin, lead, antimony and bismuth. The same graphs represent the values $\varphi_{\lambda 1}$, $\varphi_{\lambda 2}$ and $\varphi_{\lambda 3}$, calculated by the formulas (1)–(3). For the purpose of comparison

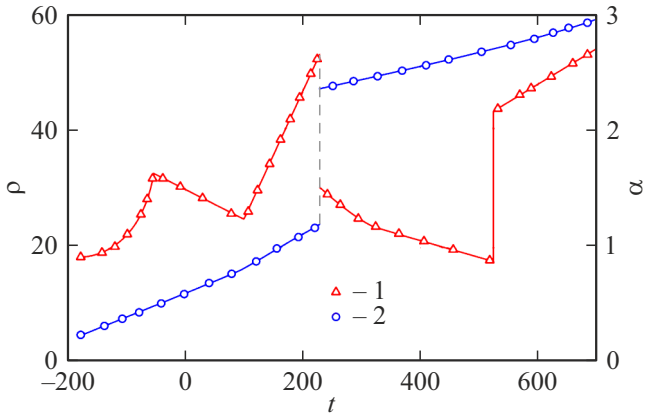

Figure 3. Electrical resistance and thermal EMF of tin [20]: *1* — α, μV/K, *2* — ρ, $\mu\Omega$·cm.

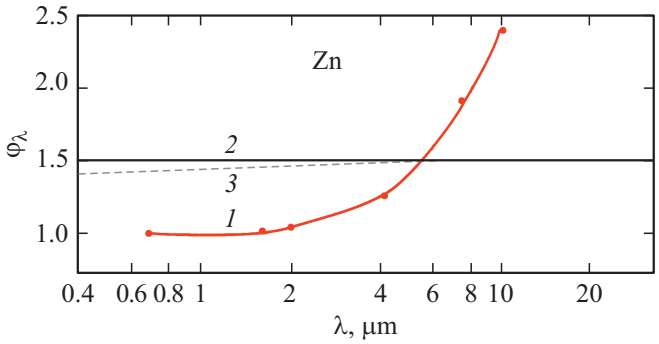

Figure 4. The values φ_λ for zinc: *1* — measurements performed by authors, *2* — calculations by the formula (1), *3* — calculations by the formulas (2) and (3).

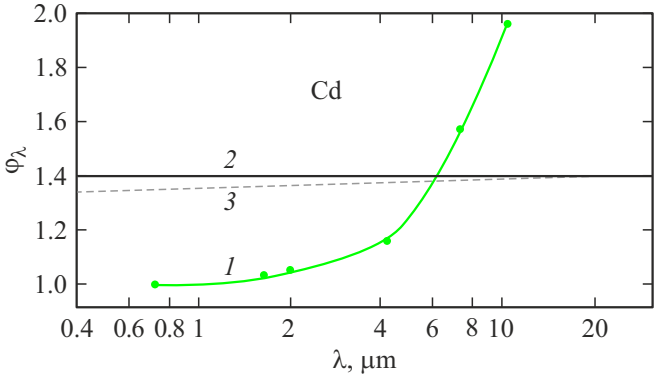

Figure 5. The values φ_λ for cadmium: *1* — measurements performed by authors, *2* — calculations by the formula (1), *3* — calculations by the formulas (2) and (3).

the line φ was drawn, corresponding to the ratio of experimental integral degrees of emissivity of solid and liquid phases. Analyses for the ratios (1)–(3), based on the Drude formula, Hagen–Rubens formula and improved Hagen–Rubens relation, give close values for the change of spectral degree of emissivity during melting (Table 3). The values $\varphi_{\lambda 2}$ and $\varphi_{\lambda 3}$ by the formulas (2) and (3) differ from each other by less than 1%, therefore, these are represented by the same line on the graphs.

Analysis in Figs. 3–6 shows that the electromagnetic theory fails to reproduce the spectral path of change of the degree of emissivity during melting not only quantitatively, but qualitatively as well. There is no emissivity degree spike in the short wavelength part of the spectrum up to the wavelengths 2–3 μm, meanwhile, according to the electromagnetic theory, for zinc, cadmium, tin and lead it reaches 40–70%; for antimony and bismuth it is negative and is 15% (antimony) and 40% (bismuth). For higher wavelengths, the values $\varphi_{\lambda 2}$ and $\varphi_{\lambda 3}$ become virtually equal $\varphi_{\lambda 1}$ and do not change together with the wavelength, meanwhile the experimental values φ_λ are growing (zinc, cadmium, tin and lead) or falling (antimony and bismuth).

Based on the experimental values φ_λ, one may assume an approximate pattern of the dependence $\varepsilon_{\lambda,liquid}$ of melts on the wavelength. In the field of short wavelengths $\varepsilon_{\lambda,liquid}$, the same as for solid metals, is approximately pro rata $\sim \lambda^{-0.5}$. As far as the λ is increased the dependence $\varepsilon_{\lambda,liquid}$ on the wavelength for liquid metals is mitigated; the value $\varepsilon_{\lambda,liquid}$ could cross the minimum value and even start growing at higher λ.

For the elements, whose degree of emissivity at melting is decreased, with the increase of λ the dependence on the wavelength will be intensified, and the degree of emissivity $\varepsilon_{\lambda,liquid}$ will fall more sharply, than in the solid phase. As a result the metals and semi-metals in liquid phase will have qualitatively different dependence $\varepsilon_{\lambda,liquid}$ on the wavelength.

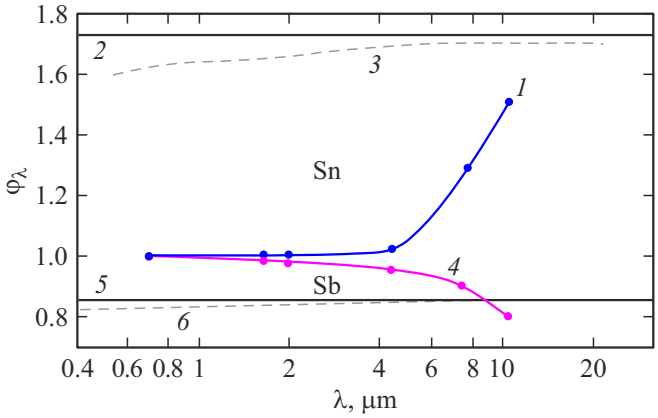

Figure 6. The values φ_λ for tin: *1* — measurements performed by authors, *2* — calculations by the formula (1), *3* — calculations by the formulas (2) and (3), for antimony: *4* — measurements performed by authors, *5* — calculations by the formula (1), *6* — calculations by the formulas (2) and (3).

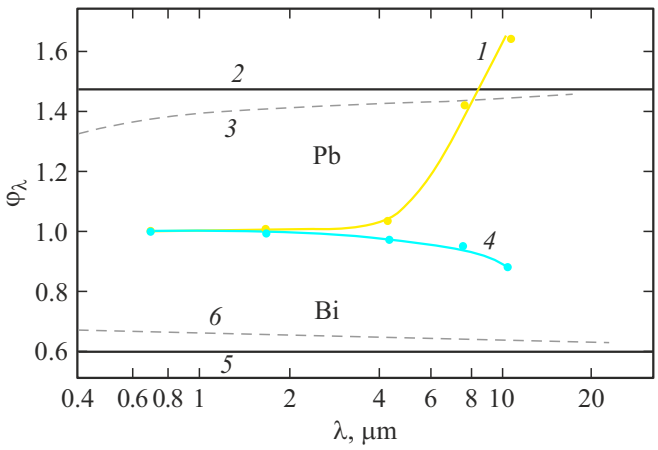

Figure 7. The values φ_λ for lead: *1* — measurements performed by authors, *2* — calculations by the formula (1), *3* — calculations by the formulas (2) and (3), for bismuth: *4* — measurements performed by authors, *5* — calculations by the formula (1), *6* — calculations by the formulas (2) and (3).

Table 3. The values $\varphi_{\lambda 1}$, $\varphi_{\lambda 2}$ and $\varphi_{\lambda 3}$, found by the formulas (1)–(3)

λ, μm	$\varphi_{\lambda 1}$	$\varphi_{\lambda 2}$	$\varphi_{\lambda 3}$	$\varphi_{\lambda 1}$	$\varphi_{\lambda 2}$	$\varphi_{\lambda 3}$
	Tin			Antimony		
0.65	1.732	1.628	1.636	0.851	0.878	0.875
1	1.732	1.646	1.631	0.851	0.874	0.870
2	1.732	1.669	1.653	0.851	0.868	0.865
4	1.732	1.690	1.688	0.851	0.863	0.860
10	1.732	1.703	1.698	0.851	0.859	0.858
15	1.732	1.708	1.705	0.851	0.857	0.856
20	1.732	1.711	1.712	0.851	0.856	0.853
	Zinc			Bismuth		
0.65	1.512	1.446	1.440	0.604	0.675	0.673
1	1.512	1.457	1.456	0.604	0.668	0.662
2	1.512	1.472	1.462	0.604	0.654	0.651
4	1.512	1.483	1.466	0.604	0.641	0.643
10	1.512	1.492	1.468	0.604	0.628	0.652
15	1.512	1.496	1.470	0.604	0.624	0.620
20	1.512	1.498	1.475	0.604	0.621	0.619
	Lead			Cadmium		
0.65	1.460	1.369	1.364	1.400	1.353	1.349
1	1.460	1.383	1.381	1.400	1.361	1.358
2	1.460	1.403	1.401	1.400	1.372	1.369
4	1.460	1.418	1.416	1.400	1.380	1.377
10	1.460	1.433	1.431	1.400	1.387	1.386
15	1.460	1.438	1.436	1.400	1.389	1.388
20	1.460	1.441	1.440	1.400	1.391	1.399

Conclusion

1. The ratios of normal spectral emissivity for a series of metals and semi-metals were experimentally obtained by using the absolute radiation method.

2. The pattern of behavior of the ratio of normal spectral emissivity to the wavelength is established for lead, tin, zinc, cadmium, bismuth, and antimony.

3. Capability of the electromagnetic theory were assessed in terms of description of the dependence of behavior of normal emissivity of metals and semi-metals at the phase transformation point. It was shown that the theory in question in the majority of cases fails to reproduce the experimental values.

Conflict of interest

The authors declare that they have no conflict of interest.

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