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Normal spectral emissivity of elements of the XI group of the periodic system

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An experimental study of the normal spectral emissivity $\varepsilon_{\lambda n}$ of chemically pure copper, gold and silver in the solid polished and liquid phases of the state, near the melting point of the metal, was carried out. The measurement of $\varepsilon_{\lambda n}$ was carried out using fixed passbands of narrowband filters. The dependence of the metal $\varepsilon_{\lambda n}$ on the wavelength in the range of the radiation spectrum of $0.26-4.2\,\mu$m microns is obtained. A comparative analysis with the literary data of other authors is carried out. The results of the calculation of $\varepsilon_{\lambda n}$ in the claimed experimental wave range according to the classical electromagnetic theory are presented

Keywords: normal spectral emissivity, wavelength, solid polished phase, liquid phase, melting point region, copper, gold, silver.

Introduction

The knowledge of the thermophysical properties of solid and liquid metals in a wide range of temperatures and wavelengths is of great scientific interest. The calculation of radiant heat transfer is needed for designing and operation of modern industrial plants [1], which determines the relevance of creating and expanding existing reference databases on the optical properties of the metals used [2–4], including emissivity in a wide range of temperatures and wavelengths.

Copper, gold and silver, which are elements of the XI group of the periodic table, have found the widest application in various technical devices and equipment. Analysis of modern periodical literature [5–7] showed that the study of optical and thermophysical characteristics of copper, silver, gold, as well as alloys based on them is relevant in the field of designing solar panel elements with a wide range of applications.

This paper presents the results of experimental determination of the normal spectral emissivity of $\varepsilon_{\lambda n}$ copper, gold and silver. The chemical purity and grades of the samples of the metals under study are presented in Table. 1.

Table 1. Characteristics of the studied metal samples

Metal	Grade	Chemical Purity, %	$T_{\text{melt.}}$, K
Copper	M 0k	99.97	1357.7
Silver	Ag 99.99	99.99	1235.1
Gold	Au 99.99	99.99	1337.3

Note. T_{melt} — melting point.

The normal spectral emissivity of these metals was studied by the radiation method [1]. The melting temperatures of metals in the experiments were close to the recommended values of the International Temperature Scale [8].

1. Experiment procedure

he measurements were carried out in an atmosphere of specially treated inert gas — argon. The normal spectral emissivity of the above metals was studied on the installation, the design of which is described in detail by the authors in [9]. The experimental method is similar to the method described by the authors in [10].

The calibration of the radiometer used was carried out according to the model of an absolute black body. The absolute black body had the shape of a cylindrical cup with a diameter of 30 mm with a wall thickness of 0.3 mm and a length of 100 mm. The model is made of alloy steel. The absolute black body served as a source of equilibrium radiation. The cylindrical cavity of the absolute black body contained five fixed diaphragms that formed a given solid angle of radiation (Fig. 1). In the inner end of the cylinder of the absolute black body there were radial grooves with a depth of 1 mm and an angle at the top 55°. These parameters of the absolute black body made it possible to obtain a degree of blackness equal to 0.99 according to [11].

It is worth noting that with the general similarity of the spectra of metal radiation with the radiation of the absolute black body, the energy scale is significantly different. The emissivity of metals is always less than one and monotonously decreases with increasing wavelength.

During calibration measurements, the absolute black body was adjusted based on the optical axis and the angle of vision of the radiometer. Temperature control along the cylinder surface of the model was carried out by mechanically fixed exemplary tungsten-rhenium thermocouples. The end effects of the model were stopped by radial screens made of molybdenum foil (Fig. 1), which made it possible to obtain a uniform temperature distribution. Absolute black body calibration was performed only when the temperature equality was reached at the specified points.

The equality of the ratio between the vignetted and the non-vignetted areas both from the melt surface and from the cavity of the mast was ensured by the use of specially made cylindrical spacers, which were used when assembling and adjusting the field of sight of the optical scheme of the radiometer.

The temperature of the studied metal (Fig. 1) was controlled by two radially located thermocouples in the near-surface layer. Thermocouples in the solid phase were mechanically inserted into the drilled channels of the near-surface layer of the metal sample. The metal was heated by an industrial frequency current.

It is known that the state of the surface significantly affects the emissivity of metals in the solid phase [12,13],
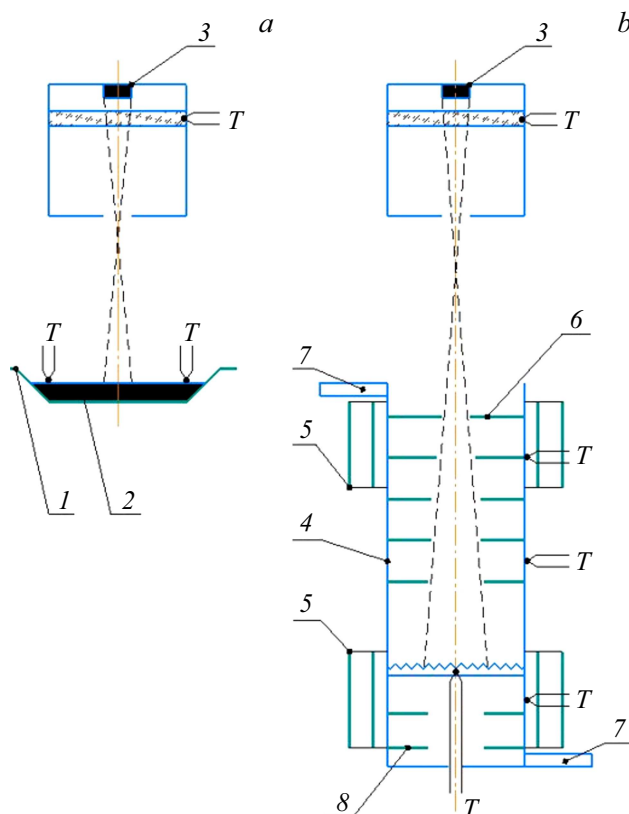

Figure 1. The principle of measuring liquid metal radiation (*a*) or an absolute black body radiation (*b*): *1* — tantalum ribbon heater; *2* — the studied metal; *3* — radiation receiver; *4* — Absolute black body housing; *5* — radial screens to compensate for end effects; *6* — radiometer viewing angle diaphragms; *7* — current leads; *8* — absolute black body heel screens.

Table 2. Spectral characteristics of the narrowband filters

Filter No.	1	2	3	4	5	6	7
Pass band of filter, μm	0.26	0.42	0.69	0.99	1.63	1.97	4.2

therefore, the surface was polished to a mirror state, when the height of the micro-dimensions on it was much less than the wavelength of the radiation under consideration, and was controlled by a non-contact profilometer. The arithmetic mean deviation of the profile over the metal surface was $0.01\,\mu$m.

The total surface area of the metal mirror of the melt was $\sim 7\,\text{cm}^2$. The sighting area from the melt surface with a radiometer according to the calculation of the optical scheme was $\sim 3\,\text{cm}^2$. The horizontal position of the radiation site obtained in the experiments was provided by the property of the liquid to spread under the influence of gravity.

The experimental error depended on temperature and was 5−8%.

The spectral radiation of metals was measured by reference points — pass bands of the used replaceable narrowband filters (Table 2).

The chemical purity of copper, gold and silver was investigated before and after the experiments in order to exclude the diffusion of the resistive heater material (tantalum tape) into the sample under study. Control measurements of the physical and chemical parameters of the samples were performed in each experiment for determining both the purity of the experiments and the additivity of the typing of experimental measurements.

The transmittance half-width of the applied dispersion filters is determined by the value of the interference order. The confidence interval of the applied filters according to the datasheet was 95% and determined the Q-factor in the transmittance of radiation.

2. Theoretical calculation and measurement results

Classical electromagnetic theory allows for a number of useful calculations of the radiation intensity for perfectly flat metal surfaces and gives simple relations between the emissivity and the electrical resistivity of the metal [14,15]. One of these relations is the Hagen−Rubens equation:

$$(\varepsilon_{\lambda n})_T = 0.365(r/\lambda)^{1/2} - 0.0667(r/\lambda) + 0.0091(r/\lambda)^{3/2},$$

where r — the electrical resistivity of the metal at the temperature of the experiment, $[\Omega \cdot \text{m}]$; λ — wavelength, $[\mu\text{m}]$.

This equation, based on the model of free electrons of the crystal lattice, allows for a theoretic calculation of the emissivity of the metal surface layer and gives a relationship between the emissivity and wavelength in the infrared
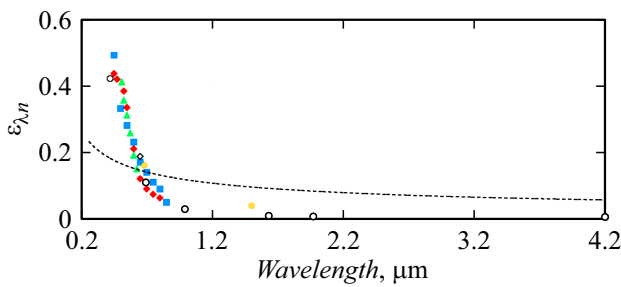
Figure 2. Dependence $\varepsilon_{\lambda n}$ of copper (solid polished phase) on wavelength: ▲ — [3] ($T_{\exp} = 1326$ K); ♦ — [19] ($T_{\exp} = 1357.7$ K); ■ — [20] ($T_{\exp} = 1357.7$ K); • — [21] ($T_{\exp} = 1357.7$ K); ◊ — [22] ($T_{\exp} = 1353$ K); ○ — the authors' measurements ($T_{\exp} = 1349$ K); dashed line — the result of the calculation using the Hagen−Rubens equation.

range [16,17], however, the discrepancy between the results of experimental data with the calculation according to classical theory can reach hundreds of percent [14].

The electric resistivity values recommended in [18] were used for calculating $\varepsilon_{\lambda n}$. A broad range of temperatures, including the melting region of copper, gold and silver is provided in this paper r.

The results of the theoretical calculation of $\varepsilon_{\lambda n}$ of the metals considered are graphically illustrated and discussed further.

The experimental data of the authors of the article, graphically presented in the figures below, are given in the form of radiation intensity values corresponding to the declared wave numbers (Table 2).

A hollow-falling curve of dependence $\varepsilon_{\lambda n}$ on the wavelength was obtained in the study $\varepsilon_{\lambda n}$ of copper in the solid polished phase (fig. 2).

The sample temperature was 1349 K. Comparison of the experimental result with works [19−22] showed satisfactory agreement in the wavelength range $0.6−0.8\,\mu$m. Studies in the range $1.5−4.2\,\mu$m revealed a further decrease of the intensity dispersion $\varepsilon_{\lambda n}$ from wavelength. The calculation performed using the Hagen−Rubens equation showed an overestimated result up to 70% in the area of short wavelengths.

The study of the liquid phase of copper was carried out at a temperature of 1362 K in the atmosphere of prepared argon used in chromatography. The intensity of $\varepsilon_{\lambda n}$ decreases with a long wave (Fig. 3). Reliable literature data [19−24] are available in a limited wave range $0.4−0.8\,\mu$m. Comparison of the experimental results with the data of these authors correlates in the confidence probability corridor within the margin of error of the experiment. The intensity dispersion $\varepsilon_{\lambda n}$ varies with the wavelength, which is explained by the presence of a mechanism for changing the intraband transition of collectivized electrons of the copper crystal lattice from one energy level to another [25]. Calculation using the Hagen−Rubens equation also showed an overestimated intensity value up to 50%,

which is explained by the inconsistency of thorium in the region of short wavelengths [14].

The intensity of $\varepsilon_{\lambda n}$ solid polished gold was studied at a temperature of 1331 K. The emissivity of gold similarly decreases with a long wave (Fig. 4) and satisfactorily coincides with the values of [3,19,21] in the wave range $0.5−1.5\,\mu$m. Further investigation of the radiation spectrum showed a steady regression of intensity $\varepsilon_{\lambda n}$ up to $4.2\,\mu$m. The theoretical calculation carried out showed an unsatisfactory correlation with the experiment. The discrepancy was up to 50% in intensity.

The liquid phase of gold in the melting point region was studied at a temperature of 1342 K. The comparison with the values [19,21,24] showed satisfactory reproduction in the wave corridor $0.6−1.5\,\mu$m (Fig. 5). A decrease of the intensity dispersion of $\varepsilon_{\lambda n}$ gold in the far infrared region was observed almost unchanged up to $4.2\,\mu$m. The theoretical calculation of the intensity of $\varepsilon_{\lambda n}$ in this case is overestimated by 70% in relation to the experimental result.

The intensity of $\varepsilon_{\lambda n}$ silver in the solid polished phase was studied under conditions similar to copper and gold. The temperature of the experiment was 1228 K. The change of $\varepsilon_{\lambda n}$ silver in the spectral range $0.26−0.69\,\mu$m satisfactorily coincided with data [19,21] (Fig. 6). The change of the
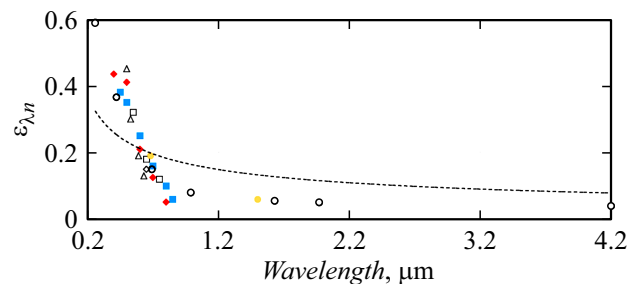

Figure 3. Dependence $\varepsilon_{\lambda n}$ of copper (liquid phase) on the wavelength: ♦ — [19] ($T_{\exp} = 1357.7$ K); ■ — [20] ($T_{\exp} = 1357.7$ K); • — [21] ($T_{\exp} = 1357.7$ K); ◊ — [22] ($T_{\exp} = 1364$ K); □ — [23] ($T_{\exp} = 1357.7$ K); △ — [24] ($T_{\exp} = 1400$ K); ○ — authors' measurements ($T_{\exp} = 1362$ K); dashed line 000 result of calculation using the Hagen−Rubens equation.
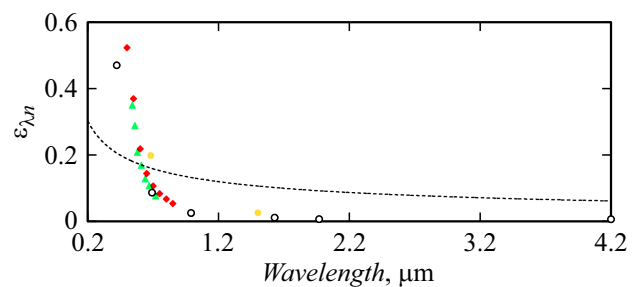

Figure 4. Dependence $\varepsilon_{\lambda n}$ of gold (solid polished phase) on wavelength: ▲ — [3] ($T_{\exp} = 1334$ K); ♦ — [19] ($T_{\exp} = 1337.3$ K); • — [21] ($T_{\exp} = 1337.3$ K); ○ — measurements by authors ($T_{\exp} = 1331$ K); dashed line — result of calculation using the Hagen−Rubens equation.

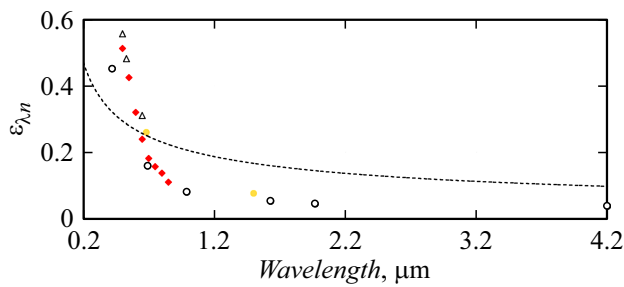**Figure 5.** Dependence of $\varepsilon_{\lambda n}$ gold (liquid phase) on wavelength: ♦ — [19] ($T_{\exp} = 1337.3\,\mathrm{K}$); ● — [21] ($T_{\exp} = 1337.3\,\mathrm{K}$); △ — [24] ($T_{\exp} = 1400\,\mathrm{K}$); ○ — the authors' measurements ($T_{\exp} = 1342\,\mathrm{K}$); dashed line — result of calculation using the Hagen−Rubens equation.

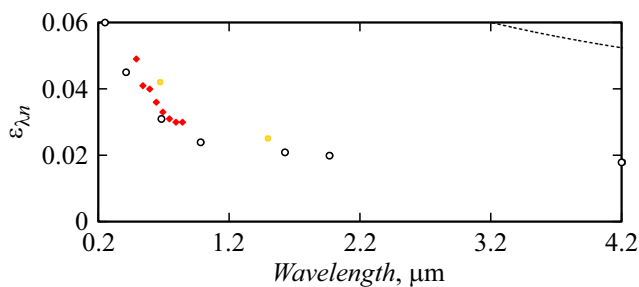**Figure 6.** Dependence of $\varepsilon_{\lambda n}$ silver (solid polished phase) on wavelength: ♦ — [19] ($T_{\exp} = 1235\,\mathrm{K}$); ● — [21] ($T_{\exp} = 1235\,\mathrm{K}$); ○ — authors' measurements ($T_{\exp} = 1228\,\mathrm{K}$); dashed line — result of calculation using the Hagen−Rubens equation.
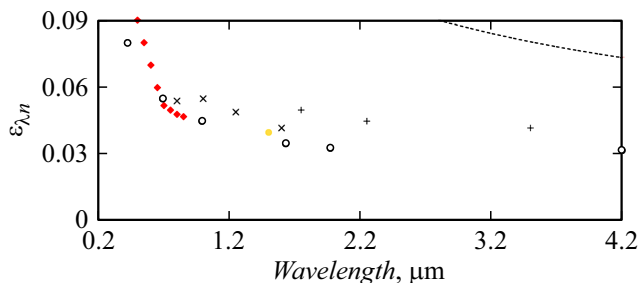
Figure 7. Dependence of $\varepsilon_{\lambda n}$ silver (liquid phase) on wavelength: ♦ — [19] ($T_{\exp} = 1235\,\mathrm{K}$); ● — [21] ($T_{\exp} = 1235\,\mathrm{K}$); × — [26] ($T_{\exp} = 1236\,\mathrm{K}$); + — [27] ($T_{\exp} = 1235\,\mathrm{K}$); ○ — authors' measurements ($T_{\exp} = 1241\,\mathrm{K}$); dashed line — result of calculation using the Hagen−Rubens equation.

intensity of $\varepsilon_{\lambda n}$ silver is observed over the entire range of spectral capabilities of the used radiometer up to $4.2\,\mu$m.

The intensity of spectral radiation for a solid metallic mirror of silver differs little from the radiation of a mirror melt, which is explained by the fact that in a metallic liquid the state of „of the near order" is preserved up to the boiling and evaporation temperatures [14].

Liquid silver was studied at the experimental temperature of 1241 K. The spectral radiation of silver (Fig. 7) changes with a long wave, which is typical for metals of this group

of the periodic system. The agreement of the experimental data with the literature sources [19,21,26,27] in the range $0.4-0.7\,\mu$m is quite acceptable, only the data on the work of [27] showed a significant difference in the intensity of radiation, which can be explained either by the chemical purity of the metal, or by the technique used in the experiment. Change of $\varepsilon_{\lambda n}$ silver can also be explained by the presence of a mechanism for the intraband transition of metal electrons.

The application of the electromagnetic theory to the calculation of the intensity $\varepsilon_{\lambda n}$ for both the solid and liquid phases of the silver state shows the general inconsistency of the theory in the field of small wavelengths. The authors explain this inconsistency by the presence of the maximum number of free electrons in the silver atom [28,29] in comparison with copper and gold — elements of the same subgroup of the periodic system.

A slight systemic discrepancy between the values of $\varepsilon_{\lambda n}$ metals both in the solid polished phase and in the liquid state is observed in the discussion of the results of comparing the experimental values obtained by the authors of the article with data from various literature sources in the UV wavelength range. The authors attribute these discrepancies to the difference in the experimental conditions of the presented researchers, namely, the degree of roughness of the surface of the solid phase of the samples, the possible presence of oxide films on the surface of the liquid phase, the percentage of the main element, research methods both by the method of heating the samples and by the instrument design of fixing thermal radiation from the surface of metals.

We partially summarized the discussed parameters of experiments of various international scientific schools are partially summarized in table 3.

In conclusion, we note that the appearance of thermal excitation of free electrons of the crystal lattice of metals is associated with a change in temperature. Due to this excitation, some of the electrons located at the highest filled energy levels move to empty levels lying above the Fermi level [30]. Thus, there the Fermi edge „is bluured" and, as a result, the overall energy transfer decreases. This circumstance can serve as an explanation for the decrease of the spectral intensity of metals with an increase of the wavelength of not only the XI group of the periodic system [31].

Conclusions

Normal spectral emissivity of copper, gold and silver samples in the solid polished and liquid phases were experimentally studied near the melting points. The measurements were performed in the wavelength range $0.26-4.2\,\mu$m using reference points — bandwidth of the applied narrowband filters.

1. The characteristic descending dependences of the intensity of the spectral radiation of $\varepsilon_{\lambda n}$ metals in the region

Table 3. Comparative research parameters $\varepsilon_{\lambda n}$

Reference to the Source	Metal	Chemical Purity of the sample	Measurement error, %	Heating method
[19]	Cu	99.994	3.9−4.5	Electromagnetic levitation
	Au	99.99	3.4−4.1	
	Ag		10−11	
[20]	Cu	99.99	10	Induction
[21]	Cu	99.996	1.5−3	Pulse
	Au	99.99		
	Ag			
[22]	Cu	99.0	6	Induction
[23]	Cu	99.9	4−5	Induction
[24]	Cu	99.999	5−6	Electromagnetic levitation
	Au			
[26]	Ag	99.9	9	Resistive
[27]	Ag	99.95	3−4	Pulse

of the change in the aggregate state on the wavelength are obtained, which is explained by an increase of the energy of the intraband electron transition. This leads to a compensatory decrease of the interband radiation caused by the broadening of the metal absorption edge and the corresponding „blurring of the" Fermi level.

2. The results obtained by the authors for $\varepsilon_{\lambda n}$ of the studied metals in comparison with the literature data have a systemic discrepancy in the UV range, which is explained by the difference in experimental methods, the chemical purity of the studied samples and the error estimate given.

Conflict of interest

The authors declare that they have no conflict of interest.

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