Journal of Engineering Physics and Thermophysics, Vol. 68, No. 2, 1995

CHANGE IN THE RADIATIVE CHARACTERISTICS OF SUBSTANCES AT PHASE TRANSITIONS

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UDC 536.3.031

An analysis of experimental investigations of the radiative characteristics of solid and liquid bodies and real gases in the vicinity of phase transitions is presented.

According to [1-4], the monochromatic emissivities of a solid and liquid metal at the melting point are identical. In [2] it is shown that in the solidification of metals there is no difference not only in the character of the spectral distribution but also in the numerical values of the emissivities. The index of refraction and the absorption coefficient in the wavelength interval 0.4–3.39 μm remain constant for solid and liquid iron, whereas for nickel they change by 10–15% [5-6]. The spectra of liquids and of their vapors differ considerably [7]. There is no unanimity of opinion on the effect of phase transitions on the radiative and optical characteristics of substances.

In [8], normal emissivities were measured for lithium, sodium, potassium, calcium, magnesium, titanium, cobalt, copper, zinc, cadmium, aluminum, indium, tin, lead, antimony, bismuth, and selenium in the solid (the surface was polished) and liquid states. Measurements were also made to obtain the radiative characteristics of water vapor (up to a pressure of 4 MPa), carbon dioxide, and certain hydrocarbons at pressures up to 10 MPa; they concern the region in the vicinity of the gas-liquid phase transition from the side of both the gas and the liquid and supercritical states.

Results of measurements and data of [9-11] that also cover the liquid phase show that the integral emissivities of metals, semimetals, and semiconductors undergo a jumpwise change upon melting (Figs. 1 and 2). The magnitude and direction of the jump are determined by the structural rearrangement of the crystal lattice that occurs. Elements that melt according to a metal-metal pattern have quite similar crystal lattices in the liquid and solid phases, with the coordination number remaining unchanged or increasing only slightly [12]. The emissivity of typical metals increases upon melting; the greatest increase in it is observed for zinc (by a factor of 2.5), cadmium (by a factor of 2.1), and copper (by a factor of 1.9).

The emissivities of bismuth, antimony, silicon, and selenium in the solid state can reach values of 0.3–0.6. The crystal lattice of these elements is rearranged considerably upon melting: weakening and elimination of covalent bonds occur, the coordination number increases up to 7–8, the number of free electrons increases by several orders of magnitude. In the liquid state these elements become metals or approach them in their properties and structure [12, 13]. Their emissivity decreases upon melting (Fig. 1). For silicon it decreases by a factor of 3.6 [10].

Among the elements investigated, calcium, titanium, and cobalt have polymorphic phase transitions in the solid state. The αCa-βCa transition at 713 K is characterized by an anomalous change in the emissivity in the form of a λ-peak (Fig. 1). The emissivity decreases by 12% at the αTi-βTi transition (Fig. 2). A jump in the emissivity of quite similar magnitude was obtained earlier for titanium [14].

Measurements in the vicinity of the α–β-transition in heating and cooling cobalt (Fig. 2, lower graph) revealed hysteresis in the behavior of emissivity as a function of temperature. This can be explained by the fact that the parameters of the αCo and βCo lattices are quite similar, and they can coexist in a rather wide range of temperatures and, consequently, there is no sharp temperature of the transition [15]. A similar hysteresis near the αCo-βCo transition is observed for the specific resistance [16]. There is another anomalous change in the emissivity of cobalt at the Curie point (Fig. 2).

Kazan State Technological University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 2, pp. 271-275, March-April, 1995. Original article submitted September 2, 1993.

1062-0125/95/6802-0237$12.50

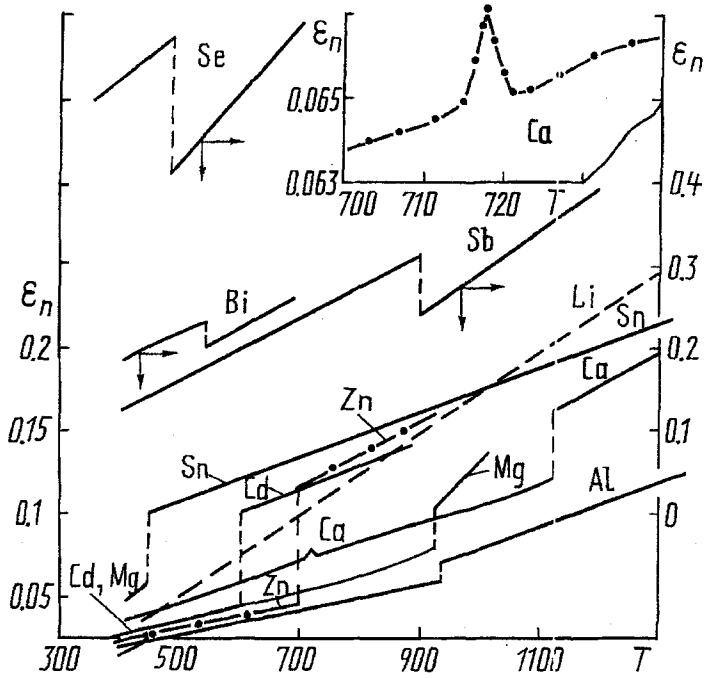


Fig. 1. Integral normal emissivities of lithium, magnesium, calcium, zinc, cadmium, aluminum, tin, antimony, bismuth, and selenium. T, K.

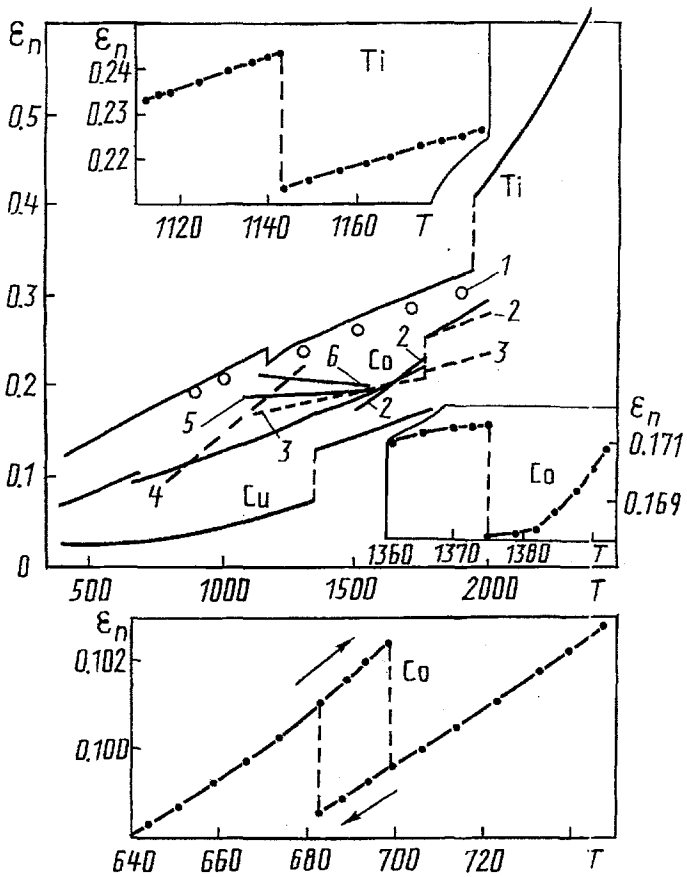
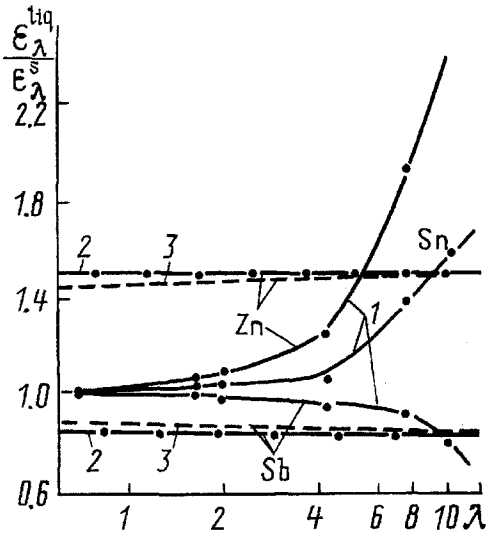


Fig. 2. Integral normal emissivities of copper, titanium (1 – data of [14]) and cobalt (2 – data of [5], 3 – [10], 4 – [20], 5 – [21], 6 – [22].

An abrupt increase in the integral emissivity was found in [17] for niobium upon transition to the superconducting state.



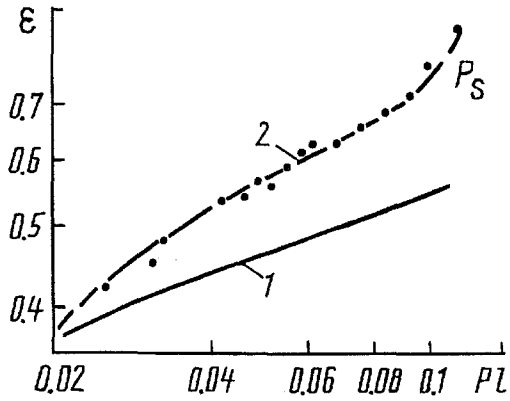


Fig. 3. Ratio between the spectral emissivities of liquid and solid zinc, tin, and antimony at the melting point: 1) experimental results; 2) calculation by Drude's formula; 3) calculation by the Hagen-Rubens formula and formula (13) from [18]. λ, μm.

Fig. 4. Integral emissivity of water vapor at 430 K: 1) l = var, P = 0.1 MPa; 2) l = 0.192 m, P = var. Pl, MPa·m.

The ratio between the normal spectral emissivities of solid and melted zinc, cadmium, tin, lead, antimony, and bismuth at the melting point was measured. Some of these measurement data are given in Fig. 3. Near the visible spectral region the metal and its melt emit radiation almost identically; the effect of the phase transition is absent. This result agrees with the available measurements in the shortwave region of the spectrum [3]. As the wavelength increases, the value of this ratio begins to deviate from unity, ascending rather sharply for metals and descending rather sharply for semimetals. The greatest change is observed for zinc, for which the greatest increase in the integral emissivity, among the elements investigated, was also obtained.

Using zinc and antimony as an example, let us now consider the possibilities of using electromagnetic theory to describe the jump in the monochromatic emissivity upon melting. Lines 2 (Fig. 3) correspond to a calculation by Drude's formula, lines 3 – by the Hagen-Rubens formula and formula (13) from [18]. The authors of [18] believe that their relation, which takes into account the finiteness of the electron relaxation time, can also be applied to liquid metals.

According to electromagnetic theory, the jumps in the emissivity amount to 50% for zinc and 15% for antimony, and they are virtually independent of the wavelength. A similar relationship between the calculations and experiment is observed for the other elements investigated. Various modifications of electromagnetic theory do not reproduce the change in the emissivity upon melting either qualitatively or quantitatively.

In [19], results are presented from works in which anomalies in the emissivity and reflectivity of iron, cobalt, and nickel were revealed at the Curie point for wavelengths of 0.5–2.6 μm .

The radiative characteristics of compressed gases change qualitatively identically with an increase in the pressure (Figs. 4 and 5). The gas-liquid phase transition is accompanied by a jump in them. The lines T = const in the supercritical region (to the right of the critical point) do not have a discontinuity, but the radiative characteristics increase sharply and almost reach values that are characteristic for the liquid.

We now consider certain regularities in the change in the radiative properties for the example of ethylene. As a function of the blackbody temperature T_0, its integral absorptivity is represented by the equation $a = 1 - \exp(-k\sqrt{\rho l})$, where $k = 1.84 \cdot \ln[-0.24(T_0/300)]$. According to the Kirchhoff law, when the temperature of the gas and the blackbody temperature are equal, the emissivity is equal to the absorptivity. The integral emissivity of ethylene found in this way (Fig. 5c), changes with pressure in the same way as the radiative characteristics considered above.

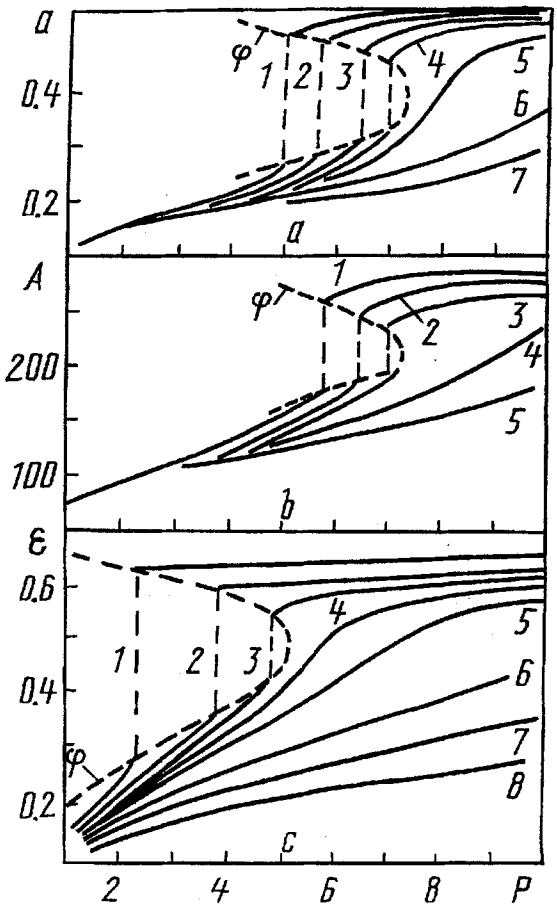


Fig. 5. Radiative characteristics of compressed gases: a) integral absorptivity of CO_2, $l = 0.025$ m; b) equivalent bandwidth 4.3 μm of CO_2, $l = 1.5 \cdot 10^{-4}$ m; c) integral emissivity of ethylene, $l = 10^{-3}$ m; φ is the boundary curve. P, MPa; A, cm^{-1}. The temperatures of the isotherms (K) are as follows:

No. of isotherm	1	2	3	4	5	6	7	8
a	228	293	298	302	306	323	343	–
b	293	298	302	313	363	–	–	–
c	250	270	280	290	300	340	400	500

The analysis of the set of experimental data for gases, liquids, metals, semimetals, semiconductors, and their melts permits us to assert unequivocally that any structural transformations occurring with solids, liquids, and gases lead to abrupt or anomalous changes in optical and radiative properties.

NOTATION

ε_n and ε, normal and hemispherical emissivities; a, integral absorptivity; A, equivalent bandwidth; T, temperature; ρ, density; P, pressure, P_s, saturation pressure; λ, wavelength; l, layer thickness. Indices: liq, liquid; s, solid; λ, spectral quantity.

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