Technical Physics, 2026, Vol. 71, No. 3

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Correlation between Emissivity and Heat Capacity of Period 4 d-Metals

© D.V. Kosenkov, V.V. Sagadeev

Kazan National Research Technological University, Kazan, Russia
e-mail: dmi-kosenkov@yandex.ru

Received September 10, 2025
Revised October 20, 2025
Accepted October 20, 2025

The relationship between total normal emissivity (ε_{tn}) and specific heat capacity (C_p) of Period 4 metals has been investigated across a temperature range encompassing a first-order phase transition (melting). A correlation analysis of these parameters was performed at homologous temperatures of C_p. A strong correlation ($R^2 > 0.97$) was established between the surface and bulk properties of the metals both below and above the melting point. However, the relative jumps in ε_{tn} and C_p at the melting point do not correlate, indicating distinct physical natures for these quantities. The presented results highlight the role of electronic structure and electron-phonon interaction in shaping the thermal properties of materials during phase transitions.

Keywords: d-metals, emissivity, heat capacity, phase transition, homologous temperature, correlation analysis.

DOI: 10.61011/TP.2026.03.63163.194-25

Introduction

Study of thermal-physical properties of metals in the neighborhood of the first-order phase transition is of great interest for the condensed matter physics and materials science [1,2]. Solid body–liquid phase transition is accompanied by a stepwise variation of key thermodynamic characteristics, including heat capacity, thermal conductivity, electrical resistance and density, reflecting fundamental rearrangement of atomic and electronic structure of a substance [3].

Analysis of relationship between energy transfer parameters — heat capacity (C_p) and total normal emissivity (ε_{tn}) measured in the infrared range, is of key importance. Heat capacity as a bulk thermodynamic property characterizes the capability of a substance to store heat energy and is related to the density of phonon states and electronic contribution at high temperatures [4]. Total normal emissivity is a surface radiation property defined by electron-phonon interaction and optical properties of the near-surface layer [5].

Importance of the study is driven by insufficient level of knowledge of correlations between bulk and surface thermal-physical properties in a wide temperature range, including the phase transition region. Period 4 d-metals characterized by complex interaction between electron and phonon subsystems and by the presence of magnetic degrees of freedom are of special interest [6].

The purpose of this study is to establish the correlation between C_p and ε_{tn} for period 4 d-metals in a temperature range, including the solid phase premelting and liquid phase superheating region. The study uses comparative analysis via homological normalization of a temperature scale, and investigation of relationship between parameters in phase transition point. The proposed approach is used for quantitative evaluation of correlation between bulk and surface thermal-physical properties and detection of the effect of electronic structure on the formation of radiation properties of metals at high temperatures.

Theoretical relevance of the study is in establishing quantitative patterns of relationship between fundamental thermal-physical properties in phase transformation conditions. Practical value of findings involves the ability to predict radiation properties of metals during high-temperature processing and creation of new materials with predefined thermal-physical properties.

1. Input data

Correlation analysis used the data for period 4 ε_{tn} d-metals. Most of the values (Ti, V, Mn, Sc, Co, Ni, Cu, Zn) were taken from the authors' experimental works. For completeness of the range, literature data for Fe were used, and ε_{tn} for Cr was calculated. Data sources for each element are detailed in Table 1.

Absolute method was used for experimental measurements of ε_{tn}. Measurements were performed in a continuous temperature range covering the $0.9 \cdot T_{melt}$ and $1.1 \cdot T_{melt}$ homologous temperature regions for each metal. Values of ε_{tn} listed in Table 2 for particular homologous temperatures were obtained by experimental data interpolation. Temperature in the experiment was controlled and measured with an accuracy of $\pm 5\,\mathrm{K}$.

The measurements used a direct vision radiometer operating in a spectral range of $1-5\,\mu$m [15] to cover the Wien radiation peak position for all given metals in this temperature range. A thermopile with platinum black coating served as a radiation receiver in the radiometer. Thus, the experimental system used in this study referred to a class of radiometric systems designed for total normal emissivity measurement. Solid phase metal samples had a mirror-finished surface. Surface roughness controlled using a

Table 1. ε_{tn} data sources and acquisition methods for

Element	T_{melt}, K [3]	ε_{tn} acquisition method	Source	$0.9 \cdot T_{melt}$, K	$1.1 \cdot T_{melt}$, K
Sc	1814	Experimental	[7]	1632.6	1995.4
Ti	1946		[8]	1751.4	2140.6
V	2220		[9]	1998	2442
Cr	2133	Calculation	–	1919.7	2346.3
Mn	1519	Experimental	[10]	1367.1	1670.9
Fe	1811	Literature data	[11]	1630	1992.1
Co	1767	Experimental	[12]	1590.3	1943.7
Ni	1728			1555.2	1900.8
Cu	1358		[13]	1222.2	1493.8
Zn	693		[14]	623.7	762.3

Table 2. Thermal-physical properties of metals at melting point and homologous temperatures

Metal	$\varepsilon_{tn}^{0.9}$	ε_{tn}^{sol}	ε_{tn}^{liq}	$\varepsilon_{tn}^{1.1}$	$C_p^{0.9}$	C_p^{sol}	C_p^{liq}	$C_p^{1.1}$
Sc	0.19	0.24	0.26	0.29	983.19	983.19	978.74	978.74
Ti	0.31	0.33	0.41	0.49	776.20	843.61	977.04	977.04
V	0.35	0.42	0.55	0.45	790.20	859.48	895.15	895.15
Cr	0.26	0.25	0.25	0.27	797.75	1591.20	975.08	975.08
Mn	0.28	0.29	0.32	0.34	744.75	842.39	873.71	873.71
Fe	0.25	0.28	0.31	0.37	678.78	760.45	823.68	823.68
Co	0.19	0.23	0.25	0.28	651.87	640.40	726.25	726.25
Ni	0.18	0.19	0.24	0.26	631.11	657.21	734.247	734.24
Cu	0.06	0.07	0.12	0.14	525.11	516.85	516.16	516.16
Zn	0.04	0.04	0.11	0.13	450.90	474.03	491.74	491.74

*Note**: ε_{tn}^{sol}, ε_{tn}^{liq} — total normal emissivity at the melting temperature for solid and liquid phases, respectively; $\varepsilon_{tn}^{0.9}$, $\varepsilon_{tn}^{1.1}$ — total normal emissivity at the homologous temperatures $0.9 \cdot T_{melt}$ and $1.1 \cdot T_{melt}$, respectively; C_p^{sol}, C_p^{liq} — specific heat capacity at the melting temperature for solid and liquid phases, respectively, [J/(kg·K)]; $C_p^{0.9}$, $C_p^{1.1}$ — specific heat capacity at the homologous temperatures $0.9 \cdot T_{melt}$ and $1.1 \cdot T_{melt}$, respectively, [J/(kg·K)].

profilometer was not higher than 0.05 μm. Measurements in the premelting region were performed in dynamic vacuum at a residual pressure lower than 10^{-3} Pa, in the liquid phase region in purified argon atmosphere. It should be noted that gas adsorption on the melt surface can affect the surface emissivity [5,16]. However, taking into account argon inertness, high measurement temperature ($\geq 1.1 \cdot T_{melt}$), reducing the adsorption level, and identical conditions for all measurements in liquid phase, the effect of adsorbed argon on experiment results is estimated as negligibly low within the method error and have no decisive action on the established correlation patterns. The error of ε_{tn} measurement was max. ±5 %. Measurement technique and experimental system are described in detail in [12].

For Cr, due to the absence of experimental data concerning emissivity in the desired temperature range, ε_{tn} was calculated using the Foote approximation [16], which is the development of the Drude and Ashkinass models, and is written as

$$\varepsilon_{tn} = 5.78\sqrt{r \cdot T} - 17.9 r \cdot T + 44(r \cdot T)^{3/2}, \qquad (1)$$

where r is the resistivity, [$\Omega \cdot$ m]; T is the temperature, [K].

Calculation used equation (1) on the basis of temperature dependences of resistance from [17]. Total error of calculation using this approximation consists of the instrumental error of input data and systematic error of the theoretical approximation.

Table 2 shows the summary of thermal-physical properties of the test materials.

Specific heat capacities of solid and liquid states listed in Table 2 were taken from an electronic guide [18]. For intermediate temperatures, linear interpolation was performed taking into account separate contributions of phases before and after melting. To smooth the differences in melting temperatures, homologous temperature range with reference points $0.9 \cdot T_{melt}$ (premelting) and $1.1 \cdot T_{melt}$ (liquid superheating) was used.

2. Discussion

First-order phase transition that accompanies the melting process is characterized by fundamental long-range order fracture in the lattice, leading to significant changes in thermal-physical and electronic properties of metals [1,2]. At a microscopic level, this takes a form of significant rearrangement of the phonon and electron state spectrum, change in the type of interatomic interactions, and transition from collective ordered atomic motion to stochastic motion typical of liquid state. These structural transformations directly affect the energy transfer mechanisms and radiative properties of metals.

Heat capacity in solid phase in a high temperature region is defined predominantly by the phonon contribution in accordance with the Debye model, however, significant contribution can be made by electronic degrees of freedom, in particular, for metals with high density of states at the Fermi level [4,6]. Additional increase in contribution from electronic degrees of freedom takes place in the liquid phase, though a change in C_p when crossing T_{melt} not always has a strongly pronounced form [3,19]. It should be noted that electron-electron interactions and magnetic degrees of freedom play a significant role for transition d-metals, which complicates theoretical description of heat capacity behavior in the phase transition region.

Emissivity is an important radiation property characterizing the ability of metal surface to emit infrared heat radiation. This quantity is defined by complex optical properties of metal and significantly depends on its electronic structure and reflectivity [5,16]. Since heat radiation processes are formed in the near-surface metal layer, but depend on bulk properties (in particular, electron mobility, density of states and electron-phonon scattering frequencies), natural physical relationship occurs between surface radiation and bulk thermal-physical properties.

Change in ε_{tn} near the melting temperature is caused by several competing mechanisms: enhancement of electron-phonon interaction, growth of the density of excited electron states, and fundamental rearrangement of the electronic structure during melting. These changes are particularly pronounced for metals with partially occupied d-shell where strong electronic correlations and complex multiband structure affect considerably the thermal behavior and radiation properties [3,19,20].

The study demonstrates that despite a different physical origin of C_p and ε_{tn} (thermodynamic and radiation, respectively), both of them are sensitive indicators of structural rearrangement of metal during first-order phase transition. Concurrent discussion of the indicators is physically justified due to the presence of a common microscopic base — changes in the electron-phonon subsystem of the metal, which explains the significant correlation at homologous temperatures that was observed statistically. The established patterns provide in-depth understanding of relationship between bulk and surface properties of metals in phase transformation conditions.

3. Analysis of correlation at homologous temperatures

Figure 1 shows the correlation between ε_{tn} and C_p for d-metals at $0.9 \cdot T_{melt}$. For quantitative evaluation of relationship, data for metals demonstrating a common trend (Ti, V, Mn, Fe, Co, Ni, Cu, Zn) was approximated by the following power function:

$$\varepsilon_{tn} = (4.26 \pm 2.15) \cdot 10^{-13} \cdot C_p^{(4.125 \pm 0.215)}. \qquad (2)$$

The obtained high coefficient of determination ($R^2 = 0.97$) proves a stable correlation and relationship between bulk and surface properties of metals in the solid phase. Metals with low C_p (Cu, Zn) demonstrate low ε_{tn}, which is caused by weak phonon processes and high reflectivity typical of metals with occupied d-shell [3]. Points of such elements as Ni, Co and Fe are grouped near the regression curve, demonstrating the predictable behavior within the established dependence. Small deviations from the common trend are observed for Sc and Cr. For Sc, wide divergence is probably attributed to characteristics of the electronic structure of Sc in the premelting region, which requires separate investigation. For Cr, for which ε_{tn} was calculated using the Foote approximation [16], deviation can be associated with limited applicability of the model for this metal. These points are shown on the curve for information only and were not included in the regression. Thus, the established dependence is statistically relevant for most of the given set of d-metals.

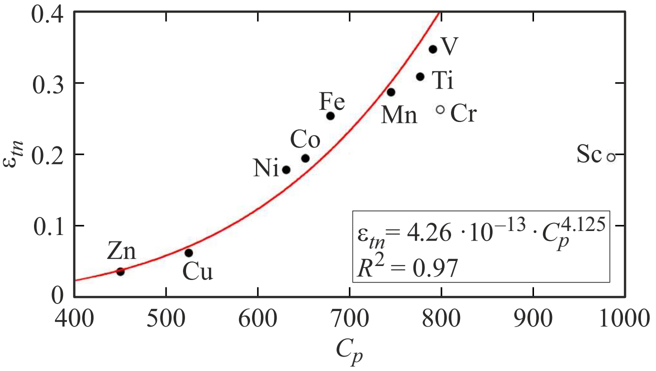

Figure 1. Correlation between ε_{tn} and C_p for metals at $0.9 \cdot T_{melt}$.

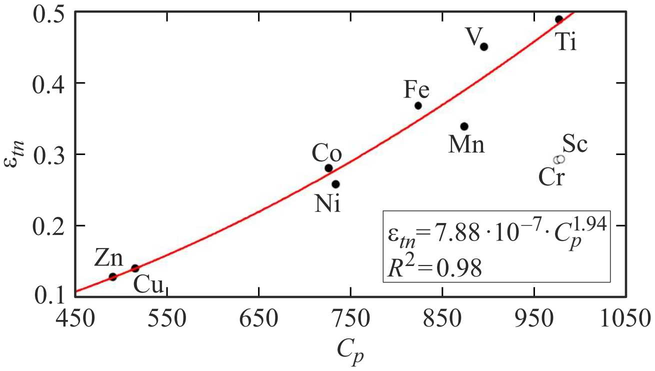

Figure 2. ε_{tn} vs. C_p for metals at $1.1\cdot T_{melt}$.

Figure 2 shows the correlation between ε_{tn} and C_p for $1.1\cdot T_{melt}$-metals at $1.1\cdot T_{melt}$. Approximation of experimental data by a power function has identified a dependence on high coefficient of determination ($R^2=0.98$):

$$\varepsilon_{tn}=(7.88\pm3.50)\cdot10^{-7}\cdot C_p^{(1.94\pm0.16)}. \qquad (3)$$

The obtained value of R^2 comparable with that for the solid phase indicates that a stable correlation between heat capacity and emissivity is maintained after melting. This demonstrates that relationship between bulk thermal-physical and surface radiation properties is fundamental and is not broken during the first-order phase transition. Metals with fully occupied d-shell (Zn, Cu) are characterized by the lowest values of ε_{tn} and C_p [3], while elements with unoccupied d-orbitals (Ti, V) demonstrate the highest values of parameters, which agrees with enhancement of electron-phonon interaction [20]. Observed deviations for Sc and Cr, data for which are shown on the curve for information only, emphasize a complex form of the influence of individual characteristics of the electronic structure (for Sc) and computational model restrictions (for Cr) on formation of radiation properties in the melt.

For interpretation of the established correlations between ε_{tn} and C_p , physical mechanisms behind these properties shall be explored. Heat capacity of metals at high temperatures is composed of the phonon and electron contributions [6]. Phonon component is induced by thermal oscillations of lattice atoms, and electron component is induced by thermal excitation of electrons near the Fermi level and is proportional to the density of electron states and temperature. Emissivity in the near-IR range is closely related to electric conductivity (Hagen–Rubens approximation [16]). Thus, ε_{tn} is defined by carrier scattering processes, from which scattering by phonons is the key one at high temperatures. Intensity of this process depends on the thermal vibration amplitude of the lattice, i.e. is directly related to the phonon contribution to heat capacity.

It should be also noted that a thermoelectronic emission effect can occur at such high temperatures due to electron emission from the heated surface [6,21]. Since the energy spectra of thermoemission electrons and of heat radiation photons partially overlap, there is potential relationship between these phenomena. To a first approximation , it is suggested that the thermoemission current contribution to the general energy balance and, therefore, to the emissivity to be determined is not predominant compared with the electron-phonon scattering mechanisms, defining optical properties in the IR range [5,16]. Nevertheless, for more restrictive quantitative separation of these contributions and building a physical model, additional studies are required.

The established stable correlation between ε_{tn} and C_p of the solid phase indicates that both parameters in crystal state are controlled by common microscopic processes. Heat capacity rise caused by enhancement of phonon modes leads to increase in resistivity due to the growth of electron-phonon scattering probability, leading to increase inε_{tn} in accordance with the Hagen–Rubens ratio [16].

High coefficient of determination ($R^2=0.98$) calculated for the liquid phase indicates that a close relationship is maintained between heat capacity and emissivity after melting. However, variation of the type of approximating dependence (compare equations (2) and (3)) reflects the fundamental rearrangement of mechanisms that define these properties. Long-range order fracture leads to a growth of phonon component of heat capacity due to appearance of new low-frequency modes. For ε_{tn}, along with electron-phonon interaction, the role of scattering from density fluctuations in the melt grows.

The statement about density fluctuations is based on the fundamental concepts of the structure of liquids. Unlike crystals, liquid metals are characterized by the absence of long-range order and the presence of significant density fluctuations, which exist now in the immediate vicinity of the melting temperature and have, in particular, the form of damped oscillations on radial distribution functions [19,22]. Heating to $1.1\cdot T_{melt}$ used in this work is sufficient for observing this effect, which is confirmed by experimental data for iron and aluminum [22] showing the variation of short-range order characteristics in this temperature range. It is the complex effect of the increased role of fluctuations and changed electron-phonon scattering that can explain the observed transformation of correlation during transition to liquid state, despite the fact that high statistical relevance of correlation is maintained.

4. Analysis of behavior of relative jumps at the melting point

Section 4 describes the analysis of the plot of dependence between the relative jumps of ε_{tn} and C_p in metals at the melting temperature T_{nmelt} (Figure 3). For clarity, the values of (C_p^{liq}/C_p^{sol}) are displaced by 0.5 unit on the y axis.

Experimental data demonstrates a wide spread of values. The largest jump of heat capacity is observed for Cr and has a negative value, which can be attributed to the characteristics of magnetic structure and electron spectrum

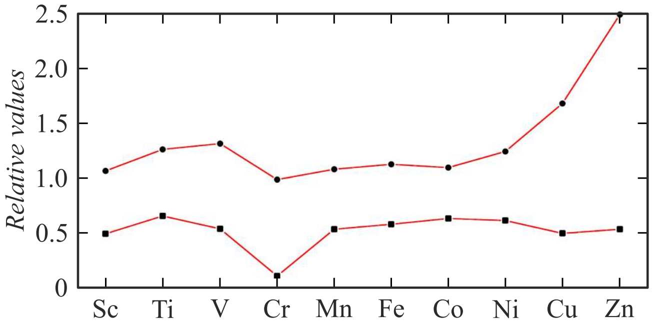

Figure 3. Dependence of relative quantities C_p^{liq}/C_p^{sol} (■) and $\varepsilon_{tn}^{liq}/\varepsilon_{tn}^{sol}$ (●) of metals on a position in the period at T_{melt}.

of this metal. Other metals of the period are characterized by positive and relatively uniform values of heat capacity jumps.

Unlike the heat capacity behavior, Cr and Mn demonstrate the lowest values of emissivity jump, while Cu and Zn show the highest values of emissivity jump. For other metals of the period, the jump of ε_{tn} has approximately the same order of magnitude.

Observed significant divergence between relative jumps of ε_{tn} and C_p indicates that there is no linear relationship between these parameters at the first-order phase transition. This phenomenon is explained by different origin of the studied properties: relative jump of C_p reflects the heat capacity variation due to lattice fracture and increase in the number of degrees of freedom [21], while the jump of ε_{tn} is defined by reflectivity variation, local rearrangement of electron density and surface layer modification [5].

Thus, the difference in microscopic mechanisms defining the behavior of heat capacity and emissivity at the melting point leads to misalignment of their relative jumps, despite the presence of correlation at temperatures deviating from T_{melt}.

Conclusions

The study has detected stable correlation between the total normal emissivity and specific heat capacity of period 4 d-metals in the homologous temperature region covering the solid body–liquid phase transition. High degree of correlation ($R^2 > 0.97$) is observed both at $0.9 \cdot T_{melt}$ in the solid phase and at $1.1 \cdot T_{melt}$ in the liquid phase, indicating the fundamental relationship between bulk and surface properties.

It has been found that the first-order phase transition was accompanied by a correlation behavior variation (a form of exponential function), while the statistical relevance of correlation was maintained. This variation is caused by the rearrangement of scattering mechanisms: electron-phonon scattering in the periodic potential prevails in the solid phase, while additional contribution in liquid is made by scattering from density fluctuations and increased role of low-frequency phonon modes.

Specific deviations from the common trend have been detected for Sc and Cr, that are attributed to the characteristics of their electronic structure and computational model restrictions, which emphasizes the importance of considering individual properties of elements. The absence of correlation between relative jumps of C_p and ε_{tn} at the melting point proves a different physical origin of changes in these parameters in phase transition, despite the presence of strong correlation near T_{melt}.

The use of homologous normalization of temperature and power approximation has proved to be effective for detecting latent patterns. The findings open the way for development of radiation property predicting methods for metals in extreme temperature conditions.

Conflict of interest

The authors declare no conflict of interest.

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Translated by E.Ilyinskaya