

# Model of Melting and Heat Transfer in Metals

E. S. Filippov<sup>1</sup>

<sup>1</sup> National Research Technological University "MISA", Moscow, Russia

Correspondence: E. S. Filippov, National Research Technological University "MISA", Moscow, Russia. E-mail: philippoves@ya.ru

Received: May 7, 2016

Accepted: May 22, 2016

Online Published: February 16, 2017

doi:10.5539/apr.v9n2p1

URL: <https://doi.org/10.5539/apr.v9n2p1>

## Abstract

Volumetric relationships under the thermal expansion of metals are analyzed. It is shown that the metals with the bcc structure possess a two-step structural change at the melting point: first, the transformation of the bcc structure to a fcc one takes place and then, liquid phase clusters with  $K = 12$  are formed. The hexagonally packed (6 + 6) layered Cd and Zn change their structure from  $K=6$  to  $K = 8$  before melting. For the polymorphic transformations fcc (hcp)  $\rightarrow$  bcc, the value of thermal expansion was sufficient to change  $K = 12$  for  $K = 8$  long before the melting point. It is assumed that at high temperatures, thermal energy transfer is associated with the exchange fluctuations: higher electron density  $+K\lambda$  and low electron density  $-K\lambda$  over the coordinate of interatomic distances, where  $\lambda = h/mc$  and  $K$  is the number of nearest neighbors.

**Keywords:** the atomic and ionic radii, the value of thermal expansion volume, the electron density fluctuation, the coordinate space, heat transfer

## 1. Introduction and Statement of the Problem

Two points essentially define the initial premises for the model - theoretical studies at high temperatures: blurring of band structure (rejection of the momentum space  $p = \hbar k$ ) and a pseudo-potential approximation of the electron-ion interaction. This makes it possible to admit the electron density fluctuations in the coordinate space  $r_a - r_i$  (here,  $r_a$  and  $r_i$  are the atomic and ionic radii, respectively), the occurrence of which we connect with the distance from the nucleus and the formation of a self-closing orbital (the circle of radius  $r$  contains an integer number of wavelengths  $2\pi r = n\lambda$ ), that is, with the formation of a standing wave from the side of  $r_i$  (ion) that, therefore, can be attributed to the maximum electron density fluctuation. On the other hand, we assume that the minimum electron density fluctuation is most remote from the nucleus  $r_a$ . Then, the maximum of the probability distribution of the electron density over the coordinate of interatomic distances at the maximum level of the electron density fluctuation  $R$  can be written as follows:

$$R = (r_a + R_c) / 2 \quad (1)$$

Where  $2\pi R_c = 2\pi r_i + \lambda_F / 2\pi$  for the self-closing orbital ( $2\pi r = n\lambda$  with the formation of a standing wave) and  $r_i$  is the crystallochemical ion radius and also:  $2\pi R = 2\pi R_c + n \lambda_F / 2\pi$ , where  $n = 2, 3 \dots$

The quantity  $R$  is defined in a pseudo-potential approximation of all of the possible combinations and shapes caused by the principles of uncertainty and the best use of the space (Filippov, 2015a,b).

As the volume of the sphere in a pseudo-potential approximation:

$$R^3 = 4/3\pi (r_a^3 - r_i^3) / K \quad (2)$$

and:

$$4/3\pi R^3 = 4/3\pi r_i^3 + r_s^3 Z, \quad (3)$$

where  $K$  is the number of nearest neighbors,  $Z$  is the number of valence electrons, and  $r_s = 1.92 \lambda_F / 2\pi$ .

As the surface of the sphere under the exchange interaction with the neighboring atoms:

$$4\pi R^2 (\lambda K) = (r_a^3 - r_i^3) Z^{1/3}, \quad (4)$$

where  $\lambda K$  is the lowest possible value in the coordinate atomic space characterizing the interaction between the neighboring atoms,  $\lambda = h/mc = 2.42 \cdot 10^{-2} \text{ \AA}$ , and  $Z^{1/3}$  is determined from  $2\pi\lambda_F = (3\pi^2 N/V)^{1/3}$  or in a monatomic approximation  $\sim Z^{1/3} / r$ .

For the liquid state, we set the quantity  $R_{SP}$  relating to the statistical packing of atoms (SP) or to a completely chaotic packing

$$R_{SP}^3 = 4/3\pi [(\sigma/2)^3 - r_i^3] / K_{SP}, \quad (5)$$

where  $r_a - R_c = (\sigma/2) - r_i$ ,  $K_{SP} = 1/12(1+2+3+\dots+12) = 6.5$  is the mean statistical number of nearest neighbors at equally probable occurrence of all coordinations from 1 to 12,  $(\sigma/2)^3 / r_a^3 = 0.65$  according to [1], and  $\sigma$  is the diameter of solid spheres in the numerical solutions of the *Percus*-Yevick equations.

Here, the criterion of adequacy of the coordination space model  $\Delta V_{xyz}$  in a pseudo-potential approximation set using Equations (1-5) is the determination of the binding energy within the model of free electrons:

$$L = (e^2/4\pi\epsilon_0) (Z/KR) \quad (6)$$

Then, we consider  $\Delta V$  in an atomic system in the thermal expansion mode when heated from 0K to  $T_{melt}$  (melting) and from 0K to  $T_{tr}$  (the polymorphic transformation fcc (hcp)  $\rightarrow$  bcc). To do this, we introduce the designations of all the reference points and volumetric relationships between them: 1). The liquid metal volume at  $T_{tr}$ :  $V_L = V_a/0.65$ , where  $V_a = 4/3\pi r_a^3$  according to Filippov (2015a); 2I. The volume at 0K:  $V_0 = 4/3\pi (1.35 - 1.47) r_a^3$  at  $K=12$  and  $K=8$ ; 3). The volume of thermal expansion from 0K to  $T_{melt}$  in a liquid phase:  $\Delta V_L = V_L - V_0$ ; 4). The volume of thermal expansion from 0K to  $T_{melt}$  in a solid phase:  $\Delta V_S = \Delta V_L - \Delta V_{melt}$ , where  $\Delta V_{melt}$  is the value of an abrupt increase of the volume at the melting point; 5). The solid metal volume at  $T_{tr}$  (at the point of the polymorphic transformation):  $V_{tr}$ ; 6). The volume of thermal expansion from 0K to  $T_{tr}$ :  $\Delta V_{tr} = V_{tr} - V_0$ , where  $V_0$  at  $K=12$ .

## 2. The Results of the Melting Modeling

### 2.1 Solid Phase at the Melting Point

We construct the melting model in the framework of the adiabatic approximation and anharmonicity of atomic thermal vibrations. In accordance with these two approximations, we search for the dimensional-volumetric characteristics associated with the destruction of the crystal lattice. From this, we have a basic assumption – the volume of thermal expansion ( $\Delta V_T$ ) from 0K to  $T_{melt}$  and the derivative of it – a linear increment  $(\Delta V_T)^{1/3}$  – we refer to the value of the anharmonicity. In this case, in the adiabatic approximation, premelting can be represented as a system of atomic spheres distorted by a quantity of  $(\Delta V_T)^{1/3}$ . The increase of this quantity must have a limit. Searching for this limit led to a quantity directly related to the pseudo-potential approximation of the electron-ion interaction:

$$(\Delta V_T)^{1/3} + r_i = r_a \quad (7)$$

Equation (7) is valid within  $\pm 3.5\%$  for 14 metals. The adiabatic assumption allows to consider it as a condition for the occurrence of the density fluctuation:  $(\Delta V_T)^{1/3} + r_i = r_a$ , the size of which corresponds to the atomic size ( $r_a$ ), that is, to the fluctuation  $K + 1$ , and thus, to the experimentally determined increase in the number of vacancies at the melting point (up to 10 atomic %  $\approx 100 [(K + 1) - K] / K$ ).

### 2.2 Liquid Phase at the Melting Point

Here,  $\Delta V_L = f(R)$ , where  $R = f(R_c, \lambda_F)$  according to Equation (1) at  $n=2,3$ , namely for metals with a bcc structure:

$$\Delta V_L = (V_L - V_0)_8 = R_{12}^3, \quad (8)$$

where  $V_0$  is determined at  $K = 8$  and  $R_{12}$  – at  $K=12$  using Equation (1).

For metals with a fcc structure:

$$\Delta V_L = (V_L - V_0)_{12} = R_{12}^3, \quad (9)$$

where  $V_0$  and  $R_{12}$  are determined at  $K=12$ .

For the hexagonally packed (6+6) layered Cd and Zn, we have:

$$\Delta V_L = (V_L - V_0)_6 = R_8^3. \quad (10)$$

Therefore, melting is preceded by a change of coordinations from  $K = 8$  to  $K = 12$  and from  $K = 6$  to  $K = 8$ . The general trend is the desire to increase the number of neighbors due to the thermal expansion. So, for metals with a bcc structure, we have:

$$R_8^3 = R_{12}^3 + \Delta V_T \quad (11)$$

For the Cd and Zn metals with a hexagonal layered packing (6 + 6), we obtain ( $\text{\AA}^3/\text{atom}$ ):

$$\text{for Zn: } R_6^3 \approx R_8^3 + \Delta V_T \rightarrow R_8^3 = R_{SP}^3 = \Delta V_L$$

[min]	[min]		[min]	[max]	
1.25	0.93	0.30	0.93	0.93	0.93

$$\text{for Cd: } R_6^3 \approx R_8^3 + \Delta V_T \rightarrow R_8^3 \approx R_{SP}^3 \approx \Delta V_L$$

[min]	[min]		[min]	[max]	[max]
1.54	1.16	0.40	1.16	1.22	1.26

where min and max are determined from the lattice periods [a] and [c].

Consequently, melting mechanism of metals both of the bcc and hexagonal structures occurs according to the two-step model.

Such structural-fluctuation mechanism is reproducible also for the polymorphic transformations fcc (hcp)  $\rightarrow$  bcc in the solid phase:

$$\Delta V_T + R_{12}^3 = R_8^3 \quad (12)$$

Here, the volume of thermal expansion together with the volume corresponding to the maximum level of the electron density fluctuation at  $K = 12$  allows to reproduce the volume fluctuations of the structure with  $K = 8$  specifically for Ti, Zr, Y, Tl, Ca, Sr, Sc, Be, and Fe.

### 3. Model of the Fluctuation-Exchange Mechanism of Heat Transfer for Solid and Liquid States.

The identified melting characteristics of the model  $R$ ,  $R_c$ ,  $r_a$ , and  $r_i$  associated with the electron density fluctuation in the coordinate space can be applied to the heat transfer model within the following assumptions: 1. The heat energy flux is associated with the electron-photon interaction and, respectively, with  $\lambda = h/mc = 2.42 \cdot 10^{-2} \text{ \AA}$ ; 2. In the electron-photon interaction, the highest possible level of the electron density fluctuation is achieved at the periphery of the atomic spheres ( $R_c$ ,  $r_i$ ,  $r_a$ ) with  $K$  neighbors, as a result of which the coordinate - atomic space has an excess  $+K\lambda$  or a deficit  $-K\lambda$  in the interaction mode (photon + electron  $\rightarrow \lambda$ ) between the emitter and detector of photons. The size of such an exchange- fluctuation cell must be limited to the value of  $\lambda_F$  or  $k_F$ . Therefore, in accordance with Equation (1), we can write:

$$R_c = r_i + K\lambda/Z \text{ and } R_c = r_i + \lambda_F / 4\pi^2 \quad (13)$$

Hence:

$$k_F = 1/2\pi [1/ (K\lambda / Z \pm n\lambda)], \quad (14)$$

where at  $n = 0, 1, 2$ , there is a complete correspondence between  $K\lambda / Z$  and  $k_F$  for the alkali and alkaline earth metals - Pb, Al, In .... (Z-valence). Justification of the  $K\lambda$  value also follows from Equation (4), where the geometric volume  $r_a^3 - r_i^3$  in the pseudo-potential approximation is practically equated to the physical volume  $4\pi R^2(\lambda K)$ .

A mirror reflection -  $K\lambda$  should correspond to the fluctuation level  $+K\lambda$  (similar to the  $2\lambda$ -model in the formation of the hcp structure, where according to Filippov (2015b), the elongation by  $2\lambda$  along the [a]-axis corresponds to the compression by  $2\lambda$  along the [c]-axis).

Hence, in the equilibrium-vibrational mode ( $R - K\lambda$ )  $\leftrightarrow$  ( $R + K\lambda$ ), we have the equality of fluxes (photon + electron  $\rightarrow \lambda$ ) of the emitter and detector. This equality of fluxes we write by the following equations using the parameter  $R$  corresponding to the maximum level of the electron density fluctuation and determined from Equation (1):

$$R + K\lambda = r_a - K\lambda / Z \quad (15)$$

$$R - K\lambda = R_c + K\lambda / Z \quad (16)$$

$$R_c = r_i + K\lambda / Z \quad (17)$$

Here, we take into account the number of valence electrons  $Z$  per photon absorption under the  $K\lambda$  exchange interaction in the range from  $r_a$  to  $r_i$ .

Equations (15-17) are fulfilled accurate to  $\pm 2\lambda$  for 14 of the metals under study: alkali and alkaline earth metals Pb, Al, In, Cd, and Zn.

For the hexagonal structure (6 + 6) Cd and Zn, we find ( $\text{\AA}/\text{atom}$ ):

$$\text{for Cd } r_a^{\max} - r_a^{\min} = 0.152 \approx K\lambda;$$

$$\text{for Zn } r_a^{\max} - r_a^{\min} = 0.140 \approx K\lambda,$$

where  $K\lambda = 6\lambda = 0.145$  and  $r_a^{\max}$  and  $r_a^{\min}$  are determined from the lattice parameters [a] and [c].

These data allow us to conclude that the value of  $K\lambda/Z$  corresponds to the maximum level of probability for the exchange interaction of conduction electrons of K atoms according to the scheme: electron + photon  $\rightarrow \lambda$ . Combining Equations (15-17) and using Equation (1), we get:

$$\begin{aligned} R - R_c &= K\lambda (1/Z + 1); \\ R - r_i &= K\lambda (2/Z + 1); \\ r_a - R_c &= 2K\lambda (1/Z + 1) \\ R_c - r_i &= K\lambda / Z; \\ r_a - R &= K\lambda (1 + 1/Z) \end{aligned} \quad (18)$$

Here, we must mark following correlation for heat transference:

$$r_a^3 = 4\pi [(R + r_i)/2]^2 K\lambda (1/Z + 1)$$

Equation (18) is valid within  $\pm 4\%$  for 12 metals.

Thus, it can be assumed that the atomic space between  $r_a$  and  $r_i$  is divided into the ready  $K\lambda$  cells, whose number could not be less than the maximum possible fluctuations of the electron density in the coordinate space. This number must be discrete for  $K\lambda$ . Therefore, the heat energy transfer (the change in the intensity of the atomic-vibrational mode) in this space is represented in the model of two fluxes exchanging by fluctuations of the electron density in the  $\pm K\lambda$  mode.

Along the radius  $R = 1/2(r_a + R_c)$  corresponding to the maximum of the electron density, two fluctuation fluxes before  $R$  and after  $R$  are separated and regulated (heating-cooling). Here,  $R$  is determined by the binding energy  $L = (e^2 / 4\pi\epsilon_0)(Z/K) 1/R$ .

Heating mode is the fluctuation flux from the atomic periphery  $r_a$  to the ionic core  $R_c$ . Cooling mode – vice versa. The equilibrium state is the compensation of the electron density fluctuations ( $\pm K\lambda$ ).

A liquid aggregate state precisely fits into this model scheme of heat transfer, since according to Equations (5, 17), we have:

$$\sigma/2 - r_i = r_a - R_c = 2 K\lambda (1/Z + 1), \quad (19)$$

where  $\sigma/2$  is a semi-diameter of the solid sphere of statistical packing of atoms (SP) defined by the relation  $(\sigma/2)^3 / r_a^3 = 0.65$ . Heating up to the boiling point changes only the ratio cluster/SP of atoms. Assuming in the superheated liquid phase near the boiling point only SP without clustering, for which  $K_{SP} = 6.5$ , we obtain:

$$\sigma/2 = R + K_{SP}\lambda \quad (20)$$

Equation (20) is fulfilled with an accuracy of 1-3% for the 14 of the studied metals.

These data for the liquid state confirm the initially assumed model of heat transfer via the exchange fluctuation quantities  $K\lambda$  between atomic spheres being in the thermal vibrational mode. Thus, for high temperatures, the maximum possible value of the electron density fluctuation is theoretically determined as  $\pm K\lambda$  and the heat transfer process is modeled as a  $\lambda$  exchange between the detector fluctuation and the fluctuation of the emitter of the photon-electron interaction.

Hence, the main conclusion is: the atomic coordinate space corresponds to the maximum possible fluctuations of electron density for the exchange of  $+K\lambda$  (emitted) by  $-K\lambda$  (absorbed) in the photon-electron interaction. This space is discrete for placing  $K\lambda$  or it is quantized by  $K\lambda$ . In general, the analysis of high-temperature processes in the coordinate space using the linear ( $R_c$ ,  $R$ , ...) and volumetric ( $R^3$ ,  $4\pi R^2\lambda K$ , ...) characteristics reveals the processes of the structure formation and phase transitions, which still did not have a simple explanation.

## References

- Filippov, E. (2015a). Fluctuation-Cluster Model of a Liquid Metal. *Russian Physics Journal*, 58(5).  
 Filippov, E. (2015b). Model of High Temperature Phase Transitions in Metals. *Russian Physics Journal*, 58(12).

## Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).