Modeling of High-Temperature Electron-Ion Interaction in Metals

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Abstract
Due to the band structure blurring, all low-temperature characteristics \( p = \hbar k \) pass to the parameter \( R \) associated with \( \lambda_F/2\pi \), binding energy, the volume of interatomic voids, the volume increment upon melting, and the packing factor. Application of the parameter \( R \) to the analysis of wave characteristics revealed their relationship with the packing factor of the reciprocal lattice (for alkali metals, it is 0.74, for Pb, Al ..., it is 0.68). A correlation is established between the fluctuation cell of heat transfer \( \pm \lambda K \) (where \( \lambda = h/mc \) and \( K \) is the number of nearest neighbors) and the reciprocal lattice of the atomic-ion space determined by the atom and ion volumes and by the parameter \( R \).

Keywords: heat transfer, atomic and ion radii, amorphous structure, cluster, density fluctuation

1. Introduction and Statement of the Problem
Blurring of the band structure is uniquely related to the increasing role of electron density fluctuations under the following unchanged characteristics of the condensed state: the Fermi energy and, respectively, the value of \( \lambda_F/2\pi \), and the binding energy \( U(r) \) and under the pseudopotential approximation of the electron-ion interaction in the coordinate space \( r_a - r_i \) (where \( r_a \) and \( r_i \) are the radii of the atom and ion). Consequently, the main assumption in the attempted simulation is the presence of the electron density fluctuations in the interstitial space characterized by the distribution of the electron density probability with respect to \( r \) in the atomic-vibrational mode.

The main task is to develop a heat transfer model, which is represented as the exchange by fluctuations of high electron density \( +\lambda K \) (emitter) and low electron density \( -\lambda K \) (receiver) in an atomic-coordinate space, which is discrete for the placement in it of cells \( \pm \lambda K \) in the interaction mode: photon + electron \( \rightarrow \lambda \) (where \( \lambda = h/mc \) and \( K \) is the number of the nearest neighbors). We believe that the development such a model adequately reflects the electron-ion interaction at high temperature.

2. Initial Data and Modeling Results
The initial data are represented by the main calculated characteristic \( R \) (the half-width of the probability distribution with respect to the coordinate \( r \) at the maximum level of the electron density fluctuation), which we find as the average value of the maximum possible values that determine the potential energy at \( r_a \) and \( r_i \approx R_c \) (minimal and maximum distances from the nucleus):

\[
R = \frac{1}{2} (r_a + R_c)
\]

In accordance with Filippov (2014), we determine the binding energy from the value of \( R \):

\[
U(r) = \left( \frac{e^2}{4\pi \varepsilon_0} \right) Z K \left[ \frac{1}{2} (r_a + R_c) \right],
\]

where \( K \) is the number of nearest neighbors, \( Z \) is the valence, and \( R_c \) is the ion core radius in metals.

On the other hand (the wave case), the value of \( R \) can be justified by the appearance of a standing wave due to the formation of a self-closing orbital (an integer number of wavelengths \( 2\pi r = n\lambda \) fit in the circle of the radius \( r \)):

\[
2\pi r = 2\pi r_i + n(\lambda F/2\pi),
\]

where for \( n = 1 \), we have \( r = R_c \), for \( n = 2 \), \( r = R \), and where \( r_i \) is the crystallochemical ion radius.

In addition, the values of \( R \) and \( R_c \), as characteristics of the level of the electron density fluctuation, are related to the atomic coordination, i.e. to the packing factor \( k = 0.74 \) and 0.68. In accordance with Filippov (2017a), we can write:
where $V_a$ and $V_v$ are the volumes of the atom and interatomic voids, respectively.

This implies:

$$k = \frac{V_a}{V_a + V_v} = \frac{r_a^3}{(r_a^3 + R^3)},$$

and

$$k = \frac{R^3}{(R^3 + R_c^3)},$$

where $V_a$ and $V_v$ are the volumes of the atom and interatomic voids, respectively.

This implies:

$$\frac{R^3}{r_a^3} = \frac{R_c^3}{R^3},$$

and

$$\frac{r_a^3}{R^3} = \frac{(1 - k)/k}{(1 - k)/k}.$$
where \( R^3 \) corresponds to the volume of the interatomic voids. Equations (11-13) are satisfied with an accuracy of \( \pm 4\% \) on average.

Analysis of Eqs. (11-13) revealed the relationship between the volumes \( V_1, V_2, \) and \( V_3 \) and the packing factor \( k \):

\[
V_3 = kV_2V_1 = V_2/k. \tag{14}
\]

Here, the value of \( k \) determined according to the atomic characteristics \( r_a, r_i, \) and \( R \) in Eqs. (11-13) for 12 metals was 0.74 and 0.68 in average, as for the fcc and bcc packages. However, according to the reciprocal lattice data, i.e., for alkali metals, it was 0.74, and for Mg, Pb, Al ..., it was 0.68.

The following relations between \( 2r_a^3, r_a^3/k = (1.47 - 1.35) r_a^3, \) and \( r_a^3 \) correspond to the value of \( k \) of the reciprocal lattice in Eqs. (11-13):

\[
2/1.35 \approx 1.47; \quad 2/1.47 \approx 1.35; \quad 1/1.35 = 0.74; \quad 1/1.47 = 0.68
\]

Thus, two forms of the atomic-ion volume - the geometric volume and the wave volume are united by the quantity \( K\lambda \).

In accordance with the uncertainty principle, either the charge \( (Z) \) must be constant at a variable \( r = 1/2 (r_{\text{min}} + r_{\text{max}}) \), or at \( r = \text{const} \), the charge should be distributed over a volume defined by \( r \) as \( Z^{1/3} \). This conclusion is realized in our data in the following two relations:

\[
4\pi R^2K\lambda = (r_a^3 - r_i^3) Z^{1/3}; \tag{15}
\]

\[
4\pi R_c^2K\lambda = R^3Z^{1/3}, \tag{16}
\]

where \( r_i \rightarrow R_c, \) since \( R_c = r_i + K\lambda/Z \) according to Eq.(3).

The accuracy of these relationships is \( \pm 5\% \) on average.

In general, there is reason to conclude that the model for the transfer of thermal energy in space from \( r_i \) to \( r_a \) can be represented as two fluxes relative to \( R \) exchanging by the fluctuations of increased (+ \( K\lambda \)) and lower (-\( K\lambda \)) electron density.

3. Consequences From the Model of Heat Transfer

3.1 Features of the heat transfer for Cu, Ag, and Au.

The values of \( r_a - r_i = 0.32 \) Å for Cu and 0.28 Å for Ag coincide with the value of \( K\lambda = 0.29 \) Å within \( \pm \lambda \). For Au, \( r_a - r_i = 0.045 \) Å corresponds to \( 2\lambda = 0.048 \) Å also within \( \pm \lambda \). These data correlate with high level of heat transfer in these metals.

3.2 Transition Metals.

Here, there is a limit in determining the values of \( R \) and \( R_c \), since s-d and d-bands of the electronic system affect \( k_F \). For example, for Ni, \( k_s = 0.55 \) a.u. (s-d band) and \( k_F = 0.81 \) a.u. (d-band), i.e., \( k_F \neq \text{const} \). However, it is possible to assume that \( R_c \rightarrow r_i \), which allows us to define \( R \) as 1/2 \( (r_a + r_i) \) and also the equality of fluctuation fluxes with the excess (+ \( K\lambda \)) and the deficit (-\( K\lambda \)) as:

\[
R - r_i = nk\lambda \pm \lambda \quad \text{and} \quad r_a - R = nK\lambda, \tag{17}
\]

where \( n = 1, 2 \).

For example, for Ni (Å/atom):

\[
R = (1.26 + 0.72)/2 = 0.99; \\
R - r_i = 0.99 - 0.72 = 0.27; \\
K\lambda = 12.0024 = 0.29.
\]

where \( 0.27 \approx 0.29 \) at \( n = 1 \).

For example, for Y:

\[
R = (1.64 + 0.88)/2 = 1.26; \\
R - r_i = 1.26 - 0.88 = 0.38; \\
2K\lambda = 2.80.024 = 0.38, \quad \text{where} \ n = 2.
\]

Equation (17) is satisfied with an accuracy of \( \pm 4\% \) for Ni, Cu, Mo, Nb, Y, Ti ... similar to Eq. (8) for the nontransition metals.
3.3 Amorphous State

We consider the quantity \(( r_a - r_i)/K\) as a dimensional criterion for the formation of an amorphous state. The main assumption is the freezing of atomic exchange between the cluster, which has \(K = 12\) or \(8\), and a chaotic packing (or an SP-statistical packing having \(K = 6.5 = 1/12 (1 + 2 + 3 + ... + 12)\), where all coordinations are equally probable Filippov, 2014, 2017a,b). This state can be defined as frozen crystallization, where not any crystallization can be developed: neither crystallization from SP, nor that from clusters under ideal conditions of heat energy removal from clusters with ordered packing and chaotic one (SP) that can be created at a distance of \((r_a - r_i)\), where the \(K\lambda\) cells can fit an integer \(n\) times:

\[
\text{for clusters:} \quad r_a - r_i = n_1 K_{\lambda}, \quad \text{for SP:} \quad \sigma/2 - r_i = n_2 K_{SP\lambda},
\]

(18)

where

\(K = 12\) or \(8\) for a cluster and \(K_{SP} = 6.5\) and \(n = 1, 2, 3, \sigma/2 = 0.867 r_a\) (Filippov, 2014, 2017a,b).

However, \(n_1 \neq n_2\). The ideal condition for the heat removal is the equality of the cells \(nK_{\lambda}\) of the cluster and SP. This equality of cells can be created with the help of composite fractions \(x, y, z\) in a combination of two or three metals, i.e., by fitting to the total integer \(n\). For example, for a pair of metals \(A\lambda B\), we have

\[
x[(r_a - r_i)/\lambda K_{12.8}]_A + \quad y[(r_a - r_i)/\lambda K_{12.8}]_B = (x, y)[(r_a - r_i)/\lambda K_{SP}]_{A,B}
\]

\(n_A n_B n_{SP}\)

\[
n_A + n_B = n_{CV} = n \quad \text{(an integer: 1, 2, 3)}
\]

The adequacy of Eq. (18) can be shown for the specific combinations of metals that lead to the amorphous phase after annealing using experimental data taken from a review article by Jonson (1986), for example, for \(Ni_{0.31}Y_{0.69}\):

\[
(0.69 \Delta r_Y + 0.31 \Delta r_Ni)/\lambda = [(0.69 \Delta r_Y)_{SP}]/\lambda
\]

\(\Sigma n = 3.2 \quad n_{SP} = 3.1 \quad n \approx 3.0.
\]

where \(\Delta r_Y = (r_a - r_i)/8; \quad \Delta r_Ni = (r_a - r_i)/12; \quad \Delta r_{SP} = (r_a - r_i)/6.5.
\]

Similarly, a number of other combinations of metals that lead to an amorphous phase after diffusion annealing or bombardment with Kr ions have been analyzed: \(Ti_{31}Nb_{22}Cu_{47}, \quad Al_{35}Nb_{65}, \quad Ni_{40}Nb_{60}\), and others. All of them are satisfied by Eq. (18) to within \(\pm 4\%\) for \(n = 1, 2, \) or 3. (the value of \(n = 3\) also follows from Eq. (9) for \(Z\) from 2 to 5). In conclusion, it should be noted a distinct parallel between the data for precious metals and the data following from Eq. (18).

References


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