The rise of liquid metals nanostructure at melting of metallic crystals

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Abstract. We present the evaluation of concentration of melting vacancies based on the model of an atomic-cluster structure of liquid metals and calculating data on their volume and energy in elementary metals. The atomic structures of liquid metals inherit essence features of a structure of crystalline precursors. The melting of crystal breaks its long-range order, and specific melting vacancies arise in the intercluster volume. The calculations show that concentration of melting vacancies is 9.9% in bcc-metals and 7.1% in hcp-metals. This means that the melting vacancies in metal crystals appear in a zone of the 2nd coordination sphere and consequently do not destroy the atom arrangement in the 1st sphere. Thus, clusters are saved, but the electronic bonds between them are changed. The obtained data confirm legitimacy of the model.

1. Introduction
Nanostructure of metallic crystals before melting most probably represents a conglomerate of micrometer and nanometer monocrystalline “islets” surrounded in intermediate volumes with non-ideal and unequal joining atomic structures. The volumes interposed between the islets filled with the same atoms, obviously have a multitude of various defects: boundary, dotty, linear, planar and volumetric: vacancies, own and impurity atoms in crystal lattice intermode, little and big pores, refractory nonmetallic particles. The real nanostructures depend on thermal and mechanical prehistory of the substance or material. However, at a moderate flow of heat to the surface of a high pure metal in spite of increasing temperature and defects concentration its equilibrium melting temperature \( T_m \) practically does not change.

2. Basic data
Many early researchers suppose that the role of vacancies in a crystal lattice is considerable at the beginning of melting [1, 2] and it is significant that specific melting vacancies \( (m\nu) \) appear during crystal to liquid transition [3, 4]. However, the concentration of vacancies in crystals before melting is low: according to various data their concentration can be from 0.01 up to 3.3%, and the estimations in [3] have shown the maximum value of 0.37%. The concentration of melting vacancies is experimentally determined in [3] to be 11% and the estimates in [4] show the value of 12% on average of metallic elements. The lowest value of the vacancy concentration is ~6% and it was received in [5]. Besides, melting vacancies differ from lattice point vacancies in volumetric characteristics. At the formation of a single crystalline vacancy some volume around the vacated unit of a lattice somewhat extends in the party of this unit, therefore quasi-free volume in the unit appears to be ~ 50 % less than
the average atomic volume \( \overline{V}_a = \overline{\tilde{V}} / N_A \), though the crystal around the vacated unit extends due to the transference of the atom to the surface of the crystal.

At the same time, it is known that later at melting the shortest atomic distances \( R_1 = 2r_a \) in many fused metals decrease in comparison with initial crystals \([3, 6]\). That can be interpreted as a consequence of relaxation process in the "islets" and as the compression of the main atomic structure around the melting vacancy. Therefore, it can be assumed that the formation of melting vacancies determines the principal mechanism and parameters of an increase in molar volume \( \tilde{V} \) at melting. The sudden change \( \Delta \tilde{V}_m > 0 \) at melting is a typical effect for the majority of metals and other substances.

If the metal has \( \Delta \tilde{V}_m < 0 \), this means that the short-range order structure of the given metal was greatly changed by melting.

3. The physical model

Our conception of the specific cluster model of the structure of simple liquid metals was stated in \([7, 8]\) and other works. The first assumption in this model is that a specific liquid cluster is a small polyatomic system consisting of the central atom and \( Z_1 \) atoms of the 1st coordination sphere. Many radiographic data about the structure of liquid metals are contradictory, but it can be assumed that the atomic short-range order in liquid and monocrystalline structures is similar \([9]\). Therefore, a \( (1+Z_1) \)-cluster can be considered as a natural elementary cell (NEC). Some NECs are the basis for the spatial construction of the crystallographic model of solids: becc, fcc, etc. Some authors suppose that for most simple metals \( Z_{1L} \), which is the first coordination number in the liquid structure at the end of melting, is equal to \( Z_{1S} \)-- the same for crystal structure at the beginning of melting at \( T_m \) \([3, 6]\).

Each of \( (1+Z_1) \)-liquid clusters is a natural elementary cell of a liquid state as well as a crystalline state. The location of \( Z_1 \) atoms around the central one may be a little different in liquid and in crystalline states due to the formation of the melting vacancy. It is necessary that in a crystal just below its melting point vacancies should be separated by the defects of structure, and in a liquid at \( T = T_m \) melting vacancies should be separated initially as self-dependent new formations similar to atomic interstitial impurities.

4. Concentrations of melting vacancies

If a compact crystalline body has the molar volume \( \tilde{V} \) and \( N_A \) atoms, it will contain the following quantity of NECs \([9]\):

\[
N_w = \frac{N_A}{1 + Z_1}.
\]

Here \( N_A \) is Avogadro number. Such a number of NECs is contained in every volume with \( N_A \) atoms (or, possibly, molecules). The quantity of atoms \( N_{Z1} \) in all the first coordination spheres of NEC is determined by the following formula:

\[
N_{Z1} = Z_1 \cdot N_w = N_A \frac{Z_1}{1 + Z_1}.
\]

It is supposed that melting vacancies should appear on the periphery of each NEC. All NECs are equitable; therefore, it is possible to assume also that only one melting vacancy is formed in each of them. It follows from this that the quantity of melting vacancies \( n_{mv} \) in each NEC is equal approximately to

\[
n_{mv} \approx \frac{N_{Z1}}{N_A} = \frac{Z_1}{1 + Z_1}.
\]

In that case the molar quantity of melting vacancies is
Having a strict estimation of the concentration of melting vacancies (5), it is possible to describe some of their characteristics (6). Thus, melting vacancies occur outside the 1st coordination sphere in bcc metals, outside each NEC. This is probable that they locate between NECs but close to them. Besides, it is possible that the order of \( x_{mv} \) values is connected with the increase of melting temperature in the series of metals Hg → bcc → fcc.

So, these conclusions support the hypothesis of the cluster structure of liquid metals as well as [7, 8].

5. Some characteristics of the melting vacancies

Having a strict estimation of the concentration of melting vacancies (5), it is possible to describe some of their characteristics on the basis of the experimental data about the molar enthalpy of melting \( \Delta H_m \) and the jump of volume at melting \( \Delta V_m \) [10]. The energy of formation of a single melting vacancy is calculated using the formula

\[
\Delta H_{mv} = \frac{\Delta H_m}{x_{mv} \cdot N_A}, \quad [J/mv] \quad \text{and} \quad \varepsilon_{mv} = \frac{\Delta H_{mv}}{x_{mv} \cdot N_A}, \quad [eV/mv],
\]

where \( \Delta H_m \) is the reference data of melting enthalpy, J/mole [11], \( \varepsilon_{mv} \) is transferring factor.

Just as (6), the volume of a single melting vacancy should be calculated as

\[
V_{mv} = \frac{\Delta V_m}{x_{mv} \cdot N_A},
\]

where \( \Delta V_m = V_l - V_S \) is the “jump” of molar volume at melting at \( T_m \).

In figures 1 to 4 the correlation of the melting enthalpy of metals \( \Delta H_m(T_m) \) and \( \varepsilon_{mv}(T_m) \) calculated using (6) on the melting vacancy and an average atom are presented. The data about melting enthalpy \( \Delta H_m \) are essentially different in various handbooks, therefore, the disorder of points concerning lines showing the dependence \( \varepsilon_{mv}(T_m) \) in bcc, fcc and some hcp metals is rather significant (the modern data from [11] apparently can be considered more reliable.) However, figure 1 shows the obvious tendency that \( \varepsilon_{mv} \) of fcc-metals is much higher than \( \varepsilon_{mv} \) of bcc metals. At the same time, it is evident that the intervals of \( T_m \) and \( \varepsilon_{mv} \) values of fcc- and bcc-metals completely intersect. That indicates their individual independence from the characteristics of the short range order nanostructure determined by the coordination number \( Z_l \). Practically the same results are observed in figures 2 to 4, representing \( \varepsilon_{mv} \) and \( \bar{E}_{mv} \) of metals having bcc, fcc and hcp structure before melting [9].

In figure 5 the review of data about the correlation between the volume of melting vacancies \( V_{mv} \), average atomic volume \( \bar{V}_a = V / N_A \), model of spherical atom \( V_a = \pi d_i^3 / 6 \) and molar volume \( \bar{V}_l \) of
Figure 1. Correlations [9] between the melting temperature and energy of nascent melting vacancies in some liquid metals (dimension [eV/mv]). The emv data here were compiled from various handbooks. 1 – fcc metals, 2 – bcc metals.

Figure 2. The energy of nascent melting vacancies in metals which have bcc structure of near order. 1 – the line representing $\Delta H_{mv}(T_m)$, [J/mv] correlation; 2 – the line representing $\Delta H_m(T_m)$, [J/atom] correlation (the data from [10]).

Figure 3. The energy of nascent melting vacancies in the metals which have fcc structure of near atomic order. 1 – the line representing $\Delta H_{mv}(T_m)$, [J/mv] correlation; 2 – the line representing $\Delta H_m(T_m)$, [J/atom] correlation (the data from [10]).

Figure 4. The energy of nascent melting vacancies in metals which have hcp-like structure of near atomic order. 1 – the line representing $\Delta H_{mv}(T_m)$, [J/mv] correlation; 2 – the line representing $\Delta H_m(T_m)$, [J/atom] correlation (the data from [10]).
Figure 5. Correlations between the molar volume of some liquid metals $V_L \text{[cm}^3\text{/mole]}$ at $T_m$ and the volume of melting vacancies $v_{mv} \text{[Å}^3\text{/mv]}$. 1, 2, 3 – some data on bcc and fcc metals: 4 – the line representing Ba, Eu; 5 – the line representing alkaline metals Cs, Rb, K, and V; 6 – the middle atomic volumes; 7 – volumes of spherical atoms [10].

liquid metals at the end of melting $L$ at $T_m$ is presented [10, 11]. As it is seen, in practically "ideal" bcc metals the lines can be considered rectilinear. The same can be also said about the Ba and Eu lines, however, the values on these two lines are essentially different. It is probable that here as well as in figure 1 this distinction is determined by deeper features of atomic structure of the metal, i.e. identity of $Z_i$ is not enough for constructing a uniform functional dependence for all ideal bcc metals and other metals having bcc structure before melting. This explains the absence of correlation between $v_{mv}$ and $v_a$ in fcc metals in figure 5.

The estimations in figure 5 show that the melting vacancies have the volume $\overline{v_{mv}}$ that sometimes exceeds the average atomic volume. (The reason for it, as well as in the case with the melting enthalpy (figures 1-4), is rather simple: the quantity of melting vacancies (4) on the order is lower than the quantity of atoms.) Therefore, it can be assumed that melting vacancies are a rather solid "new-formation" having specific internal structure. They are capable of "moving apart" liquid clusters and thus of changing the dimensional characteristic of the nanostructure of the substance. On the other hand, it is necessary to note that the large values of the relation $v_{mv} / v_a$ can mean that volume $v_{mv}$ is somewhat “smeared” near each melting vacancy, i.e. represents the volume of the zone of influence of a melting vacancy.
6. Conclusions

Many years ago Ya.I. Frenkel formulated some problems of melting physics of substances [1]. The two major questions on his list were the following:

- What is a sharp degree reduction of the order in the structure of a solid body at melting…?
- Why is melting connected to a spasmodic increase in entropy and volume…?

At present the following way of formulating these questions is preferable:

- What is the cause of an increase in molar volume at melting of most metals?
- What expands in the structure of metals or other substances at melting?

The initial conclusions from the analysis of melting model of NEC (natural elementary cells).

- A decrease in the interatomic distances at melting is a natural consequence of the process of initialization of NEC.
- An increase in the volume at melting takes place due to the phenomena outside the 1\textsuperscript{st} coordination sphere.
- Not all atoms and holes in the melt are identical in form and not all modeling volumes $v_a$, $v_{am}$, $v_{my}$ are identical in form and size.

Some possible mechanisms of volume increase at melting are the following:

- The growth of volume at melting is caused by the formation of new atom-free sites in the spatial structure of the melt which expand a NEC’s (clusters).
- The gain due to the change in the form of atoms of the 1\textsuperscript{st} coordination spheres in each NEC-cell to growth of volume of separate atoms.
- New atom-free sites appear in the electronic substructure of substances.

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