

## THEORETICAL EVALUATION OF PRESSURE AND VOLUMETRIC MODULES IN INORGANIC METALS SILICON, SELENIUM, TELLURIUM, GERMANIUM

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*Based on the double-structured model of the melt with the cluster and atomic components with the involvement of the two mechanisms of thermal clusters' decay, experimental and theoretical results on the structural states of the melts are interpreted. A possible explanation of the proposed two-structural model is in the neglect of the components of electron-ion interaction of the higher order than the second one. More over the inadequacy of pseudo-potential modification by means of the correction to the Hartee energy leads to the correct result only in the long-wave limit also. The given correlations allow us to calculate the compressibility of the melts. The theoretical calculated polyterms of the compressibility to selenium, tellurium, germanium and silicon are shown.*

**Keywords:** Cluster structure, melt, polyterms of compressibility, semiconductor, structural factor, function of radial distribution.

### Introduction

The molten metals and their alloys are widely used in the national economy. This interest is especially great in heating engineering, nuclear energy technology, electronic engineering and in the other industrial sectors, as well as for satisfaction of needs of the metallurgical production and in the engineering design of the new technology in this field. The largest attention which is devoted to the molten metals is in the metallurgy, which is conditioned by the necessity of passing the liquid phase before crystallization. The practical importance of the expected results of the work consists in the capability of using the new conceptions about the melt structure, that are based on the computer simulation technique allowing model the melt structure on the atomic level, that is important for production of the optimal for processing in the nonferrous metallurgy and the ferrous one, in pyrometallurgy on the whole, processing on the surface of phase division, also for the analogous processes in the engineering of the inorganic metals (silicon, selenium, tellurium, germanium and so forth), in addition for the nano-covers, films and other special processes.

### Theoretical part

For the calculation of the solid modules in the molted systems it is necessary to consider some correlations. Metal melts and melts of semiconductors can be considered as double-base liquid consisting of ions and electrons, then according to the virial theorem, a part of pressure which is connected with dynamics and interaction of ionic subsystem can be evaluated, i.e.

$$P_{ion} = \frac{1}{3\Omega} \left\{ 2K - \sum_{i<j} \left[ R_{ij} \frac{\partial V_{eff}(R_{ij})}{\partial R_{ij}} + R_s \frac{\partial V_{eff}(R_{ij})}{\partial R_s} \right] \right\}, \quad (1)$$

where  $K$  is kinetic energy.

For the calculation of the total pressure per to the size  $P_{ion}$  it is necessary to add the pressure, which is created by the fermi-gas that is equal to the sum of the derivative energy  $E_0(\Omega)$  и  $E_P(\Omega)$  with the opposite sign  $P_{eg} = -(\partial E_0/\partial \Omega) - (\partial E_P/\partial \Omega)$ .

The pressure  $P_{ion}$  one may rewrite in the integral form, containing explicitly dependence on the structure  $g(R)$ . If we represent the kinetic energy through the temperature, then

$$P_{ion} = \frac{1}{6\Omega} \int_0^{\infty} g(R) \left[ R \frac{\partial V_{eff}(R, R_C)}{\partial R} + R_S \frac{\partial V_{eff}(R, R_S)}{\partial R_S} \right] dR + \frac{kT}{\Omega}. \quad (2)$$

The derivative  $\frac{\partial V_{eff}}{\partial R_S}$  in the expression for pressure is specific for the melts so far as  $V_{eff}(R, R_S)$  is not only the distance function but also the function  $\Omega = \Omega(R_S)$ . It points out that the result is an effect of dielectric dependence of penetration function, which defines indirect interaction of ions from the compactness of shielding electronic subsystem  $nz$ , at the same time  $n = \frac{N}{\Omega} = \frac{3}{4\pi z R_S^3}$ . The calculation done for *Na* [1] shows that then components  $P_{ion}$  and  $P_S^0$  which are parts of the pressure  $P_{eg}$ , have the values close to zero.

If at the time of pressure estimation one neglects changes of the pair potential  $V_{eff}(R)$  of solidity, the result turns out to be overstated. It follows that in the models with stiff fixed compactness which reproduce complex  $N, Q, T$  one have to do with the great positive pressures. Such situation is observed while calculating the force coefficients in a crystal. The shown conclusion doesn't indicate the inexactness of mentioned models for a hot metal. The equilibrium should be considered simultaneously for its both subsystems – ionic and electronic, as far as the positive pressure of ionic subsystem defines bulk effects in the electronic subsystem.

As is known, in the theory of condensed systems there is “compressibility sums rule” which describes how much up-build model of the system is self-consistent. The reciprocal value of the volumetric module is equal to the mentioned compressibility. These sizes are important at the consideration of the property of condensed systems. In the crystal the quiescent volumetric module  $\beta_{st}$  equal to the second derivative energy in volume should conform to the dynamic volumetric module  $\beta_{din}$ , which is a combination of the constant elasticity, by the correlation of background dispersion by method of “long” waves [2].

Indicated correlation is defined by the interatomic interaction with the constant volume and doesn't depend on the volume-dependent components of energy. In this self-consistent model correlation between the form of the effective interaction if  $Q = const$  and derivatives of the energy in volume, containing mentioned components and defines the “compressibility sums rule”.

As is shown in the work [3], its properties are examined rather well in case of crystalline *Na*. Afterwards it appeared that the rule of sums is not fulfilled because of no self-consistency of metal model, which is built proceeding from correctness assumption of the perturbation theory on the second order by the pseudo-potential.

It gives the reason to assert that the components which emerge in the dynamic matrix in the third and fourth orders in the long-waved limit give the contribution of the second order. This inconsistency results from the inclusion of this contributions while calculating the statistic modules and neglecting them in dynamic modules. But the inclusion of these highest terms at the dynamic arraying, which correspond to the triplet and quadrupole interaction, is possible in essence [2]. Conducted calculations with the crystalline *Na* [3] have shown that for bringing into concordance of evaluable static module to the experimental  $\beta_{st}$  it is necessary to vary Hartree energy. But in such variation the dynamic module  $\beta_{din}$  having been well coordinated with the experiment turns out to be too overstated.

The feasible explanation of this is in the fact that the components of the third and the fourth orders become more important in the dynamic matrix, in the field with the little  $q$ . In the present case to preserve the consent with the experiment there is necessary the modification of the pseudo-potential itself in this mentioned field. In such case the Hartree energy variation will correspond to this modified pseudo-potential.

The statistic isothermal modulus of flexibility of the liquid phase is the following pressure derivative by volume:

$$\bar{\beta}_{st} = -\Omega \left( \frac{\partial P}{\partial \Omega} \right)_T. \quad (3)$$

The dynamic isothermal modulus is identified by the long-wave by the structural factor range  $S(q)$ :

$$\bar{\beta}_{din} = \frac{kT}{\Omega S(0)}. \quad (4)$$

Both of these modules must match in the consistency theory. However, application of the perturbation theory in the second order on the pseudo-potential and definition of the dynamic modulus through  $S(q)$  in the model with the potential that is independent on the compactness will lead to the diversions like in the case of the crystal. The exact formula for the static modulus is like this:

$$\bar{\beta}_{st} = \bar{\beta}_{ion} + \bar{\beta}_{stp}^0 + \bar{\beta}_e + \frac{kT}{\Omega}, \quad (5)$$

where

$$\bar{\beta}_{ion} = \frac{1}{18\Omega} \int D(g(R)) D(V_{eff}(R)) dR + \frac{1}{18\Omega} \int g(R) D^2 V_{eff}(R) dR,$$

where  $D$  is a statement which is input to shorten the writing:

$$D = R \frac{\partial}{\partial R} + R_s \frac{\partial}{\partial R_s}.$$

The physical value of the derivatives remains the same like in the case of the equation (2). Summing up all, one may write:

$$\bar{\beta}_{stp}^0 = \frac{1}{18\Omega} R_s \frac{\partial}{\partial R_s} R_s \frac{\partial}{\partial R_s} [V(R=0)] + P_{stp}^0, \quad (6)$$

$$\bar{\beta}_e^0 = \frac{1}{9\Omega} R_s \frac{\partial}{\partial R_s} R_s \frac{\partial E}{\partial R_s} + P_e'. \quad (7)$$

One may write the analogous formula for the dynamic modulus  $\bar{\beta}_{din}$ , as long as it is also calculated in the model with the potential independent on the compactness. Since the model is self-consistent, then the dynamic and static moduli that are calculated in it match. The analogous conclusion may be done even in the case of calculation of the crystal compressibility, which is realized in the reciprocal space. Thus, it is expected the following correlation to be accomplished:

$$\bar{\beta}_{din} = \bar{\beta}'_{ion} + kT/\Omega, \quad (8)$$

where

$$\bar{\beta}_{ion} = \frac{1}{18\Omega} \int Dg(R) \frac{R\partial}{\partial R} V_{eff} dR + \frac{1}{18\Omega} \int g(R) \frac{R\partial}{\partial R} V_{eff} dR.$$

The equation (4) gives more simple formula for  $\bar{\beta}_{din}$ . The equivalence of the equations (4) and (6) is in essence particular case of the matched condition between  $n$  and  $n+1$  the partial distribution functions. The equation (8) doesn't contain the direction to the calculation of the statistic calculation (5). However, in the calculations on the equation (5) one has to face the following problems: for the calculation such the function of the radial distribution is required  $q(R)$  which would coincide with the complete theory, i.e. for that the identity was realized:

$$S(0) = \int \{[g(R)-1]/\Omega\} dR, \quad (9)$$

equal  $\frac{kT}{\Omega\beta_{st}}$ . It requires the consideration of the components of the third and the fourth orders in the field of the minor  $q-s$ .

As these components coincide to the calculation of the effective interactions between the tree and four ions, it is an awkward task. Of course, because of this to make assumption that the function  $q(R)$ , which is calculated in the computer experiment with the double effective potential if  $Q = const$ , doesn't lead to the great mistakes, except the long-wave field. Just this very function  $q(R)$  is put in the equation (5) and (8); the equations (5) and (8) require the values of the derivatives of functions  $q(R)$  in volume which can be taken by the repetition of the computer experiment with different source compactness. The present situation is the extreme laborious task. So it is more convenient to confine with the approach:

$$g(R, R_s T) = \frac{1}{\Omega} f(R/R_s, T), \quad (10)$$

where  $f(R/R_s, T)$  is the function which provides similar change of the structure with the compactness in at the constant temperature.

However, the assumption (10) is correct for the crystal structure, but is not obligatory for a liquid. That is why this approach follows to:

$$Dg(R) = \frac{R\partial g(R/R_s)}{\partial R} + R_s \frac{\partial g(R/R_s)}{\partial R_s} = -3g(R) \quad (11)$$

Taking into account the derived result let's rewrite the equation (4) as in this way:

$$\bar{\beta}_{ion} = \frac{1}{18\Omega} \int g(R)(D^2 - 3D)V_{eff}(R) dR. \quad (12)$$

It is value for  $\bar{\beta}_{ion} = 0,097$  which has been found without variation of Hartree energy in coincide with experimental which is equal to 0,0973 as in case of the crystal. The value which is determined by the computer experiment amounts  $0,032 \pm 0,002$  that leads to  $\bar{\beta}_{abc}\Omega = 0,078 \pm 0,005$ .

## Discussion of results

The equation (10) indicates that the module taken by means of the equation (12), is “instant” volumetric modulus which, as it is shown in the work, is the upper limit of the adiabatic volumetric modulus and it bigger than isometric modulus  $Na$  for about 10%. The results which are given in the work coincide with above-mentioned ones. Besides that, the low differences are indicative of that the approach (10) is acceptable for such differences. Further one may calculate with the help of the equation (12) in the same approach. The variation of Hartee energy results 0,105 and it also coincide with the experiment, if we take into account the upper limit of the real compressibility. In case of crystalline state the correction of Hartee energy gives the considerable contribution that is necessary to achieve the concordance with the experiment.

The accuracy which is taken from the calculation as a whole is note worse than for the crystal [5] and can be explained approximately in the same way like before. One of the possible explanations applies to the substantial modification of the pseudo-potential at the low  $q-s$ , what about it was told above. It is corroborated by the calculation with the components of the third and fourth order, i.e. including the triplet and quadrupole effective interactions. It is corroborated by the calculated polyterms of adiabatic compressibility for the liquid lead (scheme 1).

Adiabatic compressibility in this process increases monotonously. Such the behavior of the compressibility basically is typical for the metal melts. Thus, one may conclude that the instantaneous dynamic modulus, which is calculated in the modulus of pair approach, is identical with the dynamic modulus, that is calculated in the complete theory on the second order, and also is distinctly differs from the static modulus, on the one hand, and from that one which is calculated in the theory of the second order, on the other hand. The first of them matches to the isometric experimental modulus, while the second one refers the correction to the Hartree energy. Thereby, the situation doesn't differ from that which was used at the analogical calculations for the crystalline condition of a substance [6].

The possible explanation is in the neglect of the components of electron-ion interaction of the higher order than the second one, also in the inadequacy of pseudo-potential modification by means of the correction to the Hartee energy, that leads to the correct result only in the long-wave limit. The given correlations allows us to calculate the compressibility of the melts. The theoretical calculated polyterms of the compressibility to selenium, tellurium, germanium and silicon are shown on the Figures 1-5. The model of the micro- heterogeneous melt with the clusters of the similar size at fixed temperature is, certainly, idealized. In fact, in the real melt there can be the clusters of various sizes. The existence of the clusters not only close to the crystallization temperature, but also at the higher temperatures, in the melts of semimetals and semiconductors is conditioned on the presence in them the two types of the chemical bond – covalent and metallic [1].

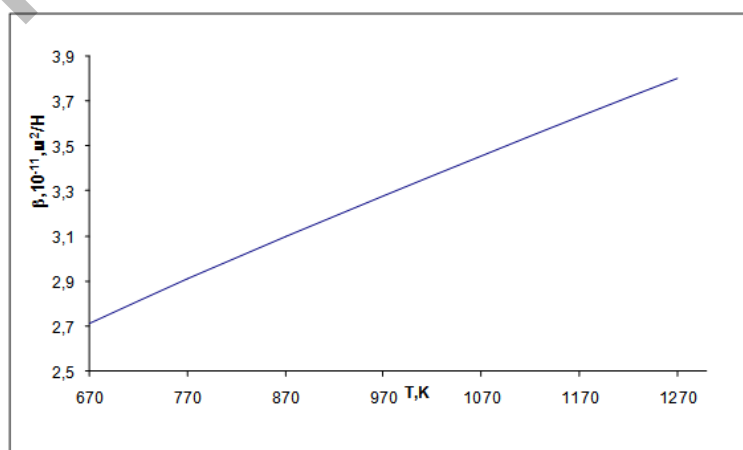


Fig.1. The compressibility polyterms of the lead melt

The covalent bond type that is present and predominant in the crystal, while its passing to the liquid condition can disappear neither just after melting, nor at the further heating. These bonds are laid on the atomic nature itself, which constitute semimetals and semiconductors in the outer electron shell of the atoms and cannot disappear completely at any aggregate substance condition.

The question only is in their manifestation degree. If these bonds exist together with the bounds that greatly differ in their energy, then they manifest essentially. The example is the molecular liquids. If these bonds are dipped into the matrix of the other bond types, which is not much differ from them energetically, then their individuality levels on the equalized background of those allied by their energy, but differ in the bond nature, for example, metallic.

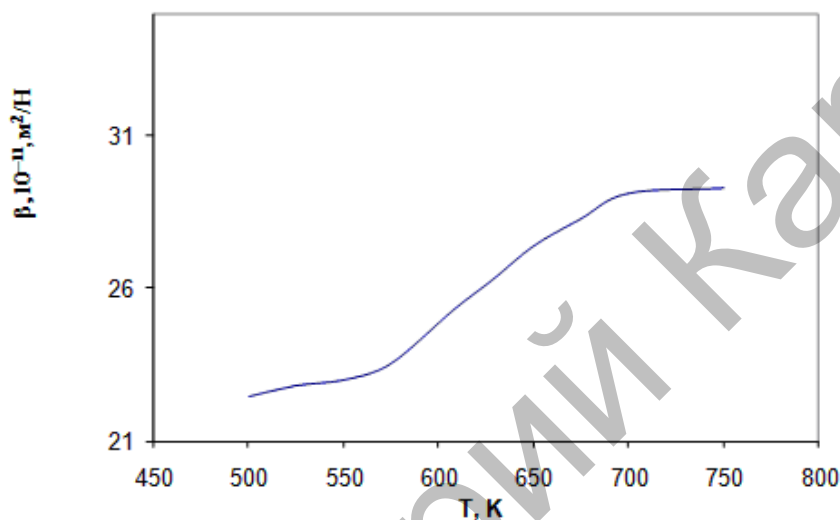


Fig.2. The compressibility polyterms of the selenium melt

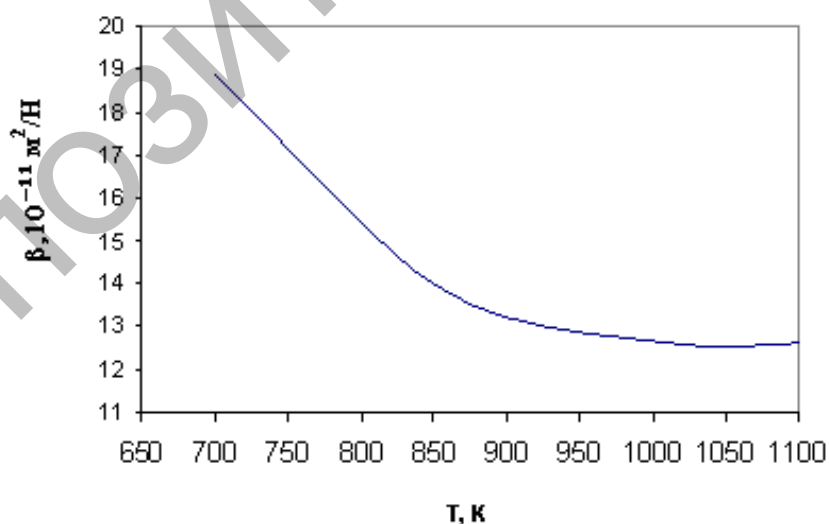


Fig.3. The compressibility polyterms of the tellurium melt

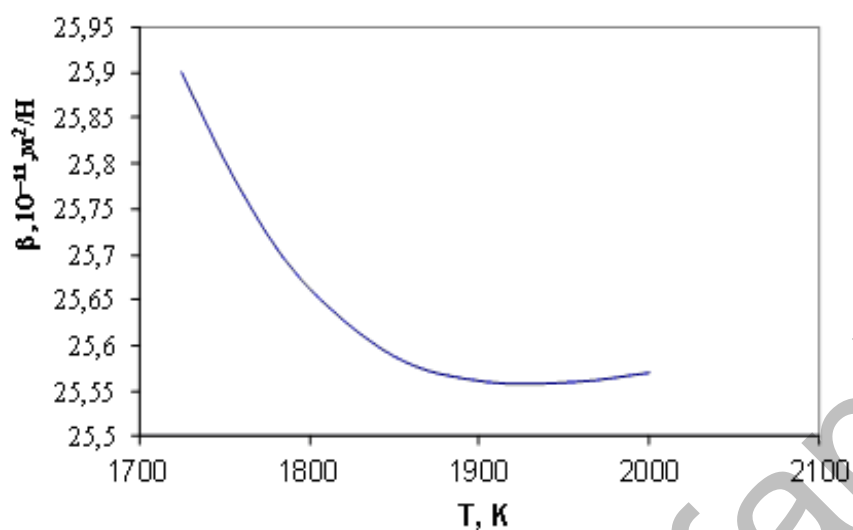


Fig.4. The compressibility polyterms of the silicon melt

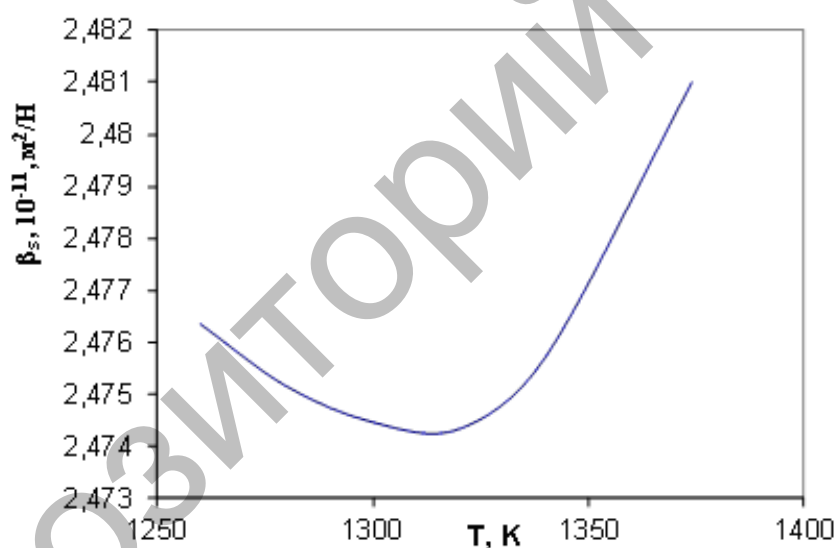


Fig.5. The compressibility polyterms of the germanium melt

To the investigations of the physicochemical melt action there is used actually almost all of the arsenals of the contemporary experimental and theoretical physics. Among the experimental methods that are applied for the investigation of the liquid condition of a liquid, the acoustic methods are in the rank of the most prospective ones and are preferential as they possess the simplicity, reliability, fast response to the change of the substance structure and the character of the interatomic interaction (in terms of the calculation of isometric compressibility of the melts, which is closely connected to the processes happening in the Bethe-Ising lattice, i.e. the transition processes order-disorder and disorder-order. Such a task was set even in 1966 by MIET Professor V.M. Glazov). Of course, we don't exclude the methods of X-ray diffraction, moreover the methods, which are based on the low angular dispersions at the neutron diffraction, as just such the methods have brought us to the beginning of the nanotechnology investigation. Nevertheless, from

the point of view of theoretical basis one of the physicochemical methods at the present moment is the quantum-chemical method, which gives an opportunity to disclose the inner structure of the extended objects in a melt. The computer systems allow realizing it though works by the low bits count, but it is not sufficient for the preliminary estimations about the microstructure of the molten substances condition.

The developmental trend of the systems approach in the physical chemistry and the related sciences required that the existing experimental and theoretical results on the thermal, thermodynamic characters of the melts were generalized on the base of the fundamental law of nature, such like Mendeleev's periodic law, with account taken of stochastic character of disordered systems.

## Conclusion

Thus, the double-structured melt cluster model (the model of the mixture of cluster and atomic component), reflecting the opportunity of equilibrium existence of the two types of chemical bond (covalent and metallic bonds), different by their nature, but close by their solidity (thermodynamic aspect) and the two mechanisms of the cluster decay (kinetic aspect) allow to explain quite right the main types of the experimental and theoretical polyterm compressibility in the melts of the semimetals and semiconductors.

The Variety of the forms of polyterms compressibility in the electronic melts requires typification, or their analysis allows to clear the mechanism of the aggregation processes and dissolution of extensive objects in the melts.

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