Change in baric properties with decreasing size of germanium nanocrystal

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Abstract. The equation of state \( P(\nu/\nu_0) \) and the baric dependences of both the lattice and the surface properties for germanium macro- and nanocrystals were calculated using the Mie-Lennard-Jones pairwise interatomic potential and the RP-model of a nanocrystal. It is shown that at a certain value of the relative volume \((\nu/\nu_0)_0\), the isothermal dependences \( P(\nu/\nu_0) \) for the macro-intersect with those for the nanocrystal. At the intersection point (at \((\nu/\nu_0)_0\)), the surface pressure becomes zero. The value \((\nu/\nu_0)_0\) decreases both with an isomorphic-isomeric rise in temperature, and with an isomorphically-isothermal decrease in the number of atoms in a nanocrystal, or with an isomeric-isothermal deviation of the shape of the nanocrystal from the energy-optimal shape (a cube for the RP-model). Based on the equation of state obtained, the change in 23 properties of Ge was studied both at an isochoric \((\nu/\nu_0) = 1\) and at an isobaric \((P = 0)\) decrease in the number of atoms in a nanocrystal at temperatures of 100, 300, and 1000 K.

1. Introduction

It is known that with a decrease in the size of a nanocrystal, its properties change [1-3]. At the same time, the baric properties as function of size are least studied. Therefore, in this work, we investigate how the change in both the state equation and the baric dependences of the lattice and the surface properties of a germanium nanocrystal depends on size.

As a rule, experimental study of size dependences is carried out in isobaric conditions [1], i.e. when the pressure in the system is constant: \( P = \text{const} \). At the same time, in most cases the theoretical calculations are carried out for the isochoric process, i.e. at constant density: \( R = \text{const} \) [1-3]. This is due to the fact that in an experiment it is difficult to maintain constant density of a nanocrystal, and in theoretical models it was difficult to determine the surface pressure, and therefore the state equation of the nanocrystal. In this regard, the following questions arise.

(i) How large is the difference in the change of a particular property with the isochoric and with the isobaric reduction of the nanocrystal size?

(ii) What properties change slightly at isochoric or isobaric change in nanocrystal size?

Therefore, in this work, we will investigate the change of the various properties of germanium, for both isochoric and isobaric decreases in the number of atoms in a nanocrystal.

2. Method of calculating the nanocrystal properties

To calculate the properties of a nanocrystal of a simple one-component substance, it is necessary to determine both the interaction potential of a pair of its atoms and the calculation method that is based on this potential. Let the pairwise interatomic interaction in a crystal of a single-component substance
be described by Mie-Lennard-Jones potential, which has the following form [4, Ch. 3]:

$$\varphi(r) = \frac{D}{(b-a)} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^a \right],$$  \hspace{1cm} (1)

where $D$ and $r_0$ are the depth and coordinate of the potential minimum, $b > a > 1$ are the numerical parameters.

Then, using the “only-nearest-neighbors interaction” approximation, the Debye temperature as a function of the first coordination number and the distance between the centers of the nearest atoms can be determined as follows [4, Ch. 2; 5]:

$$\Theta(k_n, c) = A_n(k_n, c) \xi \left[ \frac{1}{1 + \left( \frac{8D}{k_B A_n(k_n, c) \xi^2} \right)^{1/2}} \right],$$  \hspace{1cm} (2)

Here $k_B$ is the Boltzmann constant, function $A_n$ emerges when the energy of “zero vibrations” of atoms in a crystal is factored in, $k_n$ is the first coordination number depending both on the nanocrystal size and the shape of its surface [4, Ch. 6], $c = (6k_B v \pi)^{1/3}$ is the distance between the centers of the nearest atoms, $v = V/N$ is the specific volume, $V$ and $N$ is the volume and the number of atoms in a nanocrystal:

$$A_n(k_n, c) = K_n \frac{5k_n ab(b+1)}{144(b-a)} \left( \frac{r_0}{c} \right)^{b+2}, \hspace{1cm} K_n = \frac{\hbar^2}{k_B^2 m}, \hspace{1cm} \xi = \frac{9}{k_n(\infty)},$$  \hspace{1cm} (3)

where $m$ is the atomic mass, $\hbar$ is the Planck’s constant, $k_n$ is the structure packing ratio, $k_n(\infty)$ is the first coordination number in the volume of the nanocrystal.

If the “only-nearest-neighbours interaction” approximation is applicable for a nanocrystal with Gibbs geometrical surface, the dependence of the nanocrystal energy on size and shape will be determined by the size and shape dependence of the average (across all nanocrystals) value of the first coordination number. In this case, using the Einstein model for the nanocrystal vibrational spectrum, the following expression can be applied for the specific (per atom) Helmholtz free energy of a nanocrystal [4, 6]:

$$f_H(k_n,c,T) = \left( \frac{k_n}{2} \right) D U(R) + 3k_B \Theta_E(k_n,c) \left( \frac{1}{2} + \left( \frac{T}{\Theta_E(k_n,c)} \right) \ln \left[ 1 - \exp \left( - \frac{\Theta_E(k_n,c)}{T} \right) \right] \right),$$  \hspace{1cm} (4)

where $\Theta_E$ is the Einstein temperature, which is related to the Debye temperature through the equation [6]: $\Theta = (4/3)\Theta_E$. $R = r_{dc}$ is the relative linear density of a crystal, the potential energy function in accordance with (1) is equal to:

$$U(R) = \frac{aR^b - bR^a}{b - a}.$$

Let us assume that $k_n$ as function of size and shape of a nanocrystal with a Gibbs surface does not depend on density ($R$) and temperature but is determined only by the number of atoms in the nanocrystal ($N$), its shape parameter ($f$) and constant $k_n(\infty)$ and $k_n$. Then from (4) for the state equation ($P$) and isothermal modulus of elasticity ($B_T$) the following equations can be obtained [7]:

$$P = -\left( \frac{\partial f_H}{\partial v} \right)_T = \frac{k_n}{6} D U'(R) + 3k_B \Theta_E \cdot \gamma' \cdot E_w \left( \frac{\Theta_E}{T} \right) \left( \frac{1}{v} \right),$$  \hspace{1cm} (5)

$$B_T = -v \left( \frac{\partial P}{\partial v} \right)_T = P + \left[ \frac{k_n}{18} D U''(R) + 3k_B \Theta_E \cdot \gamma' \cdot \gamma - q \right] E_w \left( \frac{\Theta_E}{T} \right) - 3N \cdot k_B \cdot \gamma^2 \cdot T \cdot F_E \left( \frac{\Theta_E}{T} \right) \left( \frac{1}{v} \right).$$  \hspace{1cm} (6)

The following functions are introduced here:

$$E_w(y) = 0.5 + \frac{1}{\exp(y) - 1}, \hspace{1cm} F_E(y) = \frac{y^2 \exp(y)}{[\exp(y) - 1]^2},$$

$$U'(R) = R \left( \frac{\partial U(R)}{\partial R} \right) = \frac{ab(R^b - R^a)}{b - a}, \hspace{1cm} U''(R) = R \left( \frac{\partial U'(R)}{\partial R} \right) = \frac{ab(bR^b - aR^a)}{b - a}. $$  \hspace{1cm} (7)
From (2) it is easy to find the expressions for the first (γ), second (q) and third (z) Grüneisen parameters:

\[ \gamma = \left( \frac{\partial \ln \Theta}{\partial \ln v} \right)_T = \frac{b + 2}{6(1 + X_w)} , \quad q = \left( \frac{\partial \ln \gamma}{\partial \ln v} \right)_T = \frac{X_w(1 + 2X_w)}{(1 + X_w)} , \]

where the function: \( X_w = A_w \xi / \Theta \), which determines the role of quantum effects, is introduced.

Since the Debye temperature (2) does not depend on the temperature during isochoric heating, the isochoric and isobaric heat capacities can be defined as [6]:

\[ C_v = 3N \cdot k_B \cdot F_E \left( \frac{\Theta_E}{T} \right) , \quad C_p = C_v (1 + \gamma \alpha_p T) , \]

where the isobaric coefficient of thermal volume expansion can be calculated using the Grüneisen equation [6]:

\[ \alpha_p = \left( \frac{\gamma}{k_u} \right) \frac{C_v}{k_u \cdot N \cdot B_T [\pi c_0^3 / (6k_B)]} v_0 / v , \quad v_0 = \frac{\pi r_3^3}{6 k_p} . \]

A correction factor is introduced here: \( k_u = \gamma / \gamma_C \). It emerges due to the fact that the “frequency” Grüneisen parameter (which is calculated from the Debye temperature using (8)) may deviate from the thermodynamic Grüneisen parameter \( \gamma_C \) (which is calculated from thermodynamic data in (10)) [8, 9].

From (4) and (5) it is also possible to calculate the values of the integral chemical potential (i.e. Gibbs specific energy): \( g = F_E + P \cdot v \) and the specific entropy of the system:

\[ s = \left( \frac{\partial f}{\partial T} \right)_v = 3k_B \left[ \frac{1 - \exp \left( \frac{\Theta_E}{T} \right)}{\left( \exp \left( \frac{\Theta_E}{T} \right) - 1 \right)} \right] . \]

The obtained expressions (2)-(10) allow us to determine the dependence of the state equation as well as the indicated properties on the normalized volume \( v/v_o = (clr_3)^3 = R^3 \) and temperature \( T \) for a single-component nanocrystal with given structure (i.e. at the given values of \( k_o(\infty) \) and \( k_p \)), provided that we know the parameters of the interatomic potential (1) and the functional dependence of the first coordination number on the size and shape of the nanocrystal, i.e. function \( k_o(N, f) \).

Let us note that if we take: \( N \rightarrow \infty, V \rightarrow \infty \) at \( v = V/N = \text{const} \), and \( k_o(N, f) = k_o(\infty) \), both the equation of state, and the baric dependences of the indicated properties for macrocrystal can be calculated using the formalism from (2)-(10). This method was successfully applied in calculating the properties of macrocrystal for iron, diamond, silicon, germanium [7] and molybdenum [10].

### 3. RP-model of nanocrystal

To determine the function \( k_o(N, f) \), we use the RP-model of a nanocrystal [4, 11]. The RP model is essentially the following: suppose that a nanocrystal with a Gibbs free surface has the form of a rectangular parallelepiped with a square base, faceted with (100) faces. The value of \( f = N_p / N_po \) is the shape parameter, which is determined by the ratio of the number of atoms on the side edge \( N_p \) to the number of atoms on the edge of the base \( N_{po} \). For a rod shape we have \( f > 1 \), for a cube \( f = 1 \), for a nanocrystal of the plate-like shape \( f < 1 \). The number of atoms in a nanocrystal, equal to: \( N = f N_{po}^3 / \alpha \), varies within the range: \( 2^0 / \alpha \leq N \leq \infty \), where \( \alpha = \pi / (6 k_p) \) is a structure parameter.

Restricting the system with a surface will lead to the disconnection of bonds at the border. Therefore, if the “only-nearest-neighbors interaction” approximation is used, instead of the first coordination number \( k_o(\infty) \), we must take the average (across all nanocrystals) value of the first coordination number \( k_o(N, f) \), which depend both on \( N \) and on \( f [4, 11] \). The structure of the system (characterized by the packing factor \( k_p \)) is assumed to remain unchanged: \( k_p = \text{const} \).

Within the RP-model framework, the dependence of the normalized average value of the first coordination number on the size (\( N \)) and the shape of the nanocrystal takes the following form [4, 11]:
\[ k_{n}^{*} = \frac{k_{n}(N, f)}{k_{n}(\infty)} = 1 - Z_{s}(f) \left( \frac{\alpha^2}{N} \right)^{1/3}, \]  

(11)

where \( k_{n}(\infty) = k_{n}(N = \infty) \) is the first coordination number for the macrocrystal,

\[ Z_{s}(f) = \frac{1 + 2f}{3f^{2/3}}. \]  

(12)

The shape-function \( Z_{s}(f) \) reaches unity at \( f = 1 \), i.e. at a cube shape. For plate-like \((f < 1)\) or rod-like \((f > 1)\) shapes, the value of \( Z_{s}(f) \) is greater than one. Therefore, the function \( k_{n}(f)^{s} \) for any value of \( N \) has the maximum at \( f = 1 \), i.e. for the most energetically optimal, the cubic shape of a rectangular parallelepiped.

The volume and surface area for the RP-model are equal:

\[ V = N \rho_{c} f c^3 = N \alpha c^3, \quad \Sigma = 6 c^2 \alpha (N \alpha)^{2/3} Z_{s}(f), \]

where \( \alpha \) is the coefficient with the packing density of atoms on the nanocrystal face (i.e. in the surface layer) factored in: \( \alpha = \alpha^{2/3} \). It is evident that the volume of the nanocrystal \( V \) does not depend on the shape of the system, i.e. on the value of \( f \).

In the RP model framework, for the specific (per unit area) surface energy of the \((100)\) face of the nanocrystal \( \sigma(N, f) \), its isochoric and isobaric derivatives with respect to temperature, and for the surface pressure \( P_{sf} \), the following equations can be obtained [4, Ch. 6; 11]:

\[ \sigma(N, f) = -\frac{k_{n}(\infty)D R^{2}}{12\alpha^{2/3} r_{0}^{2}} L_{E}(N, f), \]  

(13)

\[ \sigma'(T)_{v} = \left( \frac{\partial \sigma}{\partial T} \right)_{c,N,f} = -\frac{3 k_{b} R^{2} \gamma(N, f)}{2 \alpha^{2/3} (b+2) r_{0}^{2}} k_{n}(N, f)^{*} F_{E} \left( \frac{\Theta_{E}}{T} \right), \]  

(14)

\[ \sigma'(T)_{p} = \sigma'(T)_{v} + v \cdot \alpha_{p} \left( \frac{\partial \sigma}{\partial v} \right)_{T,N,f} = \sigma'(T)_{v} + \frac{2}{3} \sigma \cdot \alpha_{p} \cdot \Delta_{p}, \]  

(15)

\[ P_{sf} = \left[ \frac{\partial (\sigma \Sigma / N)}{\partial v} \right]_{T,N} = P_{ls} (1 - \Delta_{p}), \]  

(16)

where the Laplace pressure \( P_{ls} \) and the functions introduced are as follows:

\[ P_{ls} = \frac{\Sigma}{3V} \sigma = \frac{4\alpha_{s} Z_{s}(f)}{(\alpha N)^{1/3} c}, \]  

(17)

\[ L_{E}(N, f) = U(R) + 3H_{w}(N, T), \]  

(18)

\[ \Delta_{p} = -\left[ \frac{\partial \ln(\sigma)}{\partial \ln(c)} \right]_{T,N,k_{p},f} = 1 + \frac{1}{2L_{E}(N, f)} \left( \frac{U'(R) - q - \gamma \cdot t_{y} \left( \frac{\Theta_{E}}{T} \right)}{(\gamma \cdot t_{y} \left( \frac{\Theta_{E}}{T} \right))} \right), \]  

(19)

\[ H_{w}(N, T) = \frac{6 \gamma(N, f)}{(b + 2)} \left[ \frac{k_{b} \Theta_{E}(N, f)}{D k_{n}(N, f)} \right] E_{w} \left( \frac{\Theta_{E}}{T} \right), \]  

\[ t_{y}(y) = 1 - \frac{2y \exp(y)}{[\exp(2y) - 1]}. \]  

(20)

At the positive value of \( P_{sf} \) the surface pressure compresses the nanocrystal, as is usually assumed. Obviously, in the “thermodynamic limit” \((N \to \infty \) and \( V \to \infty \) with \( v = V/N = \) const), the functions \( P_{ls} \) (17) and \( P_{sf} \) (16) disappear because in this case \( k_{n}(N \to \infty) \to 1 \), and the equations (13)-(15) are transformed into the formulae for a macrocrystal. At \( T \to 0 \) K, the functions in (14) and (15) tend to zero for any \( N \), which is consistent with the third law of thermodynamics in Planck’s “strong” formulation. Note that the surface pressure can also be found from (5) as the difference between pressures calculated for macro- and nanocrystals:

\[ P_{sf} = P(T, v, N = \infty) - P(T, v, N, f). \]  

(21)

Thus, the function \( k_{n}(N, f) \) obtained in the RP-model framework together with the formalism (2)-(20) allow us to calculate the dependence of all lattice and surface properties on the size and shape of the nanocrystal at given temperature and specific volume.
4. The calculations of germanium properties

Germanium, chosen for calculations (m(Ge) = 72.59 a.m.u.), has a diamond structure: \( k_0(\infty) = 4 \), \( k_p = 0.3401 \). The parameters of the pairwise interatomic potential (1) were defined in [4, Ch. 3; 12] and were tested in [7, 11, 12]:

\[
r_0 = 0.245 \text{ nm}, \quad b = 4.3, \quad a = 2.75, \quad D_b/k_B = 46764.12 \text{ K}, \quad D_i/k_B = 22511.76 \text{ K}.
\]

Here \( D_b \) is the depth of the potential, which is used to calculate the properties under the elastic (reversible) deformation of a covalent crystal, and \( D_i \) is the depth of the potential to calculate the properties of the crystal during its plastic (irreversible) deformation.

**Figure 1.** Isothermal-isomorphic dependencies of pressure vs. relative volume for macro- (curves 1 and 2) and nano- (curves 3 and 4) of a Ge crystal. Curves 1 and 3 are 1000 K isotherms and curves 2 and 4 are 300 K isotherms.

**Figure 2.** Isothermal-isomorphic dependence of the elasticity modulus vs. pressure for macro- (curves 1 and 2) and nano- (curves 3 and 4) of a Ge crystal. Curves 1 and 3 are 300 K isotherms and curves 2 and 4 are 1000 K isotherms.

Figure 1 shows the isothermal-isomorphic dependences of pressure on the normalized volume \((v/v_o)\) for germanium calculated using the elastic-type potential (i.e., with the depth \(D_b\)) and Eq. (5). Curves 1 and 3 are 1000 K isotherms and curves 2 and 4 are 300 K isotherms. In Figure 1, curves 1 and 2 are obtained for a macrocrystal, and curves 3 and 4 are the isomorphic-isometric (at constant \(f\) and \(N\)) dependencies for a nanocrystal of \(N = 223\) atoms with a cubic shape of the Gibbs surface, i.e. at \(N_{po} = 7\) and \(f = 1\).

We compared the dependence of \(P(v/v_o, T, N = \infty)\) calculated in this way with the experimental data for the germanium macrocrystal in [7]; therefore, we will not do this here. A decrease in the pressure growth during the transition from a macro- to a nanocrystal indicates a decrease in the elastic modulus: \(B_T = -v(\partial P/\partial v)_T\) as size decreases (figure 2). The decrease in \(B_T\) with the decrease in the nanocrystal size was demonstrated in [2, 11, 13-16]. Note that the surface pressure calculated using Eq. (16) to the third decimal place coincided with the result obtained from Eq. (21). This also confirms the correctness of this method for calculating the equation of state of a nanocrystal.

It is evident from figure 1 that at a certain value of the relative volume \((v/v_o)_{ho}\), the isothermal dependences of \(P(v/v_o)\) for the nanocrystal and macrocrystal intersect. Thus, at \((v/v_o)_{ho}\) the surface pressure becomes zero: \(P_g(v/v_o)_{ho} = P(\text{Macro}) - P(N = 223, f = 1) = 0\), consequently: \(\Delta_P(v/v_o)_{ho} = 1\). At \((v/v_o)<(v/v_o)_{ho}\) the surface pressure compresses the nanocrystal \((P_g > 0)\), and at \((v/v_o)>(v/v_o)_{ho}\) the nanocrystal stretches by means of the negative surface pressure: \(P_g < 0\).

Table 1 shows the coordinates of the “zero surface pressure” point, i.e. where \(P_g = P(\text{Macro}) - P(N = 223, f = 1) = 0\) obtained with the elastic potential (i.e., with the depth \(D_b\)) for a cubic Ge
nanocrystal of \( N = 223 \) atoms (i.e. \( N_{po} = 7, f = 1 \)). The calculations showed that the value of \((v/v_0)_0\) decreases with the isomorphic-isomeric (i.e. \( f \) and \( N \) – const) temperature increase, or with the isomorphic-isothermal (\( f \) and \( T \) – const) decrease of \( N \), or under isomeric-isothermal (\( N \) and \( T \) – const) deviation of the nanocrystal shape from the most energy-optimal shape (a cube for the RP-model).

| Table 1. Coordinates of the “zero surface pressure” point for a cubic Ge nanocrystal of \( N = 223 \) atoms. |
|---|---|---|---|
| \( T, K \) | \( R_0 = r_d/c_0 \) | \((v/v_0)_0\) | \( v(P_f = 0), \text{cm}^3/\text{mol} \) | \( P_0, \text{GPa} \) |
| 100 | 0.99930 | 1.0021 | 13.6632 | 0.20748 |
| 300 | 0.99970 | 1.0009 | 13.6468 | 0.57456 |
| 1000 | 0.99993 | 1.0002 | 13.6373 | 1.92078 |

It follows also from figure 1 that the pressure in the nanocrystal passes through zero at the value of \( v/v_0 \) greater than that of the macrocrystal. It means that at an isobaric (at \( P(\text{Macro}) = P(N=223, f=1) = 0 \)) decrease in the number of atoms, the nanocrystal becomes more stretched by negative surface pressure. Therefore it is far from correct to assume that with an isobaric decrease in the number of atoms, the density of the nanocrystal is preserved. Moreover, the farther from the point of zero surface pressure the value of the isobar pressure is, the more the nanocrystal density will vary with an isothermal-isomorphic decrease in its number of atoms.

It should be noted that an increase in the interatomic distance with a decrease in diamond and silicon nanocrystal size was detected by M.Ya. Gamarnik in 1990 [17, 18]. From his results, some authors made the erroneous conclusion that there is no surface pressure in the nanocrystal. But as it was shown by us in [4, 19, 20], and as it can be seen from figure 1, the surface pressure \( (P_f) \) in the nanocrystal is not zero. But \( P_f \) is always less than the surface pressure calculated by the Laplace formula: \( P_f < P_a \), and under certain conditions, the surface pressure from (16) can change the reverse the sign: \( P_f > 0 \).

Tables 2–4 present the lattice and surface properties calculated by the above method (they indicated in the first column) for germanium at \( T = 100, 300, \) and \( 1000 \) K, respectively. In Columns 2 and 3 the absolute values of the macrocrystal properties are shown for the isochore \( v/v_0 = 1 \) and for the isobar \( P = 0 \), respectively. Columns 4 and 5 show the relative (to the corresponding values for a macrocrystal) property values for a cubic nanocrystal of \( N = 223 \) atoms \( (N_{po} = 7, f = 1) \), both for isochore \( v/v_0 = 1 \) and for isobar \( P(N) = 0 \).

The correction factor \( k_o \) was determined by comparing the calculated \( \alpha_p(\text{calc}) \) and the experimental \( \alpha_p(\text{exp}) \) values of the thermal expansion coefficient of a germanium macrocrystal at \( T = 300 \) K and \( P = 0 \) as: \( k_o = \alpha_p(\text{calc})/\alpha_p(\text{exp}) \). Using the data from [21]: \( \alpha_p(\text{exp}) = 17.1 \times 10^{-6} \) \( 1/\text{K} \), we obtained: \( k_o = 1.354 \). In the calculations, the value of \( k_o \) was assumed to be independent from the temperature, pressure, and the number of atoms in the nanocrystal.

Calculations of the surface energy and its derivatives were carried out on the basis of the plastic potential, i.e. with depth \( D_v \). This is due to the fact that when measuring the surface energy of a crystal, the covalent bonds are irreversibly disconnected [4, 7, 11, 12].

The pressure derivatives were calculated by numerical differentiation of this parameter by pressure along the isotherm.

The dependence of the Poisson ratio on the size of the nanocrystal at different temperatures was calculated from (22):

\[
\mu_p(N,T) = \frac{1}{2} \frac{1}{48 \cdot X_c(N,T) \cdot [\gamma(N)]^2}, \quad X_c(N,T) = \frac{\sigma(N,T)}{c \cdot B_f(N,T)}. \quad (22)
\]

For some properties of a germanium macrocrystal at \( T = 300 \) K and \( P = 0 \) the following experimental estimates are found in the literature:

- \( \Theta/K = 373.3 – 374 \) [4], 372 – 398 [23], 372 – 376 [24], 362 – 376 [25];
- \( \gamma = 1.05 \pm 0.03 \) [4, 26];
- \( \gamma_c = 0.4 – 0.5 \) [27], 0.75 [28], 0.492 – 0.76 [29];
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$B_i/\text{[GPa]} = 72.43$ [30] – 77.2 [31]; $B'(P)_b = 3.0$ [32] – 4.55 [33];
$\alpha_p/[10^{-6} \text{[1/K]} ] = 17.1$ [21] – 17.7 [34]; $C_p/(Nk_b) = 2.815$ – 2.824 [23];
$\sigma(100)/[10^{-3} \text{[J/m}^2]\text{]} = 800 – 1940$ [4], 1000 – 1710 [35];
$\mu_p = 0.199 – 0.209$ [36] – the Poisson's ratio for polycrystalline;
$\mu_p(i, j) = 0.156 – 0.358$ [36] – for different directions of monocrystal.

From table 3 it can be seen that our calculations for a macrocrystal agree well with these estimates. We note that some characteristics calculated here for a germanium macrocrystal were estimated for the first time, since in their case there are still no estimates in the literature even at $T = 300 \text{K}$ and $P = 0$.

We mean isothermal pressure derivatives for functions: $\Theta$, $\alpha_p$, $C_p$, $C_p$, $\sigma(100)$, as well as for isochoric and isobaric temperature derivatives of function $\sigma(100)$.

### Table 2. The calculated properties of Ge (listed in Column 1) at $T = 100 \text{K}$.

| Property [unit] | Macro $N = \infty$ | Nano $N = 223 (N_{pc} = 7, f = 1)$ |
|-----------------|---------------------|-------------------------------------|
| $v = \frac{V}{N} = [\pi/(6k_b)]c^3 \text{[cm}^3\text{/mol]}$ | $R = r/c = 1$ | $P = 0$ | $X(N, R=1)(X(\infty))$ | $X(N, P=0)(X(\infty))$ |
| $P = 0.3655 \text{GPa}$ | $0.9984$ | $0.3323 \text{GPa}$ | $0.9981$ |
| $0.0333 \text{GPa}$ | $0.0600 \text{GPa}$ |

$\Theta$ is the Debye temperature [K]
$\gamma = – (\partial \ln \Theta)/(\partial \ln V)_T$
$\eta = 10^{-3}[(\partial \ln \Theta)/(\partial \ln V)]_T 10^3$
$z = – (\partial \ln q)/(\partial \ln V)_T$
$B_T = – V(\partial P)/(\partial V)_T \text{[GPa]}$
$B'(P) = (\partial P)/(\partial T)_V$ $\text{[10^{-3} K^{-1}]}$
$\alpha_p = \gamma C_v/(k_B T) \text{[10^{-6} K^{-1}]}$
$\alpha_p = \gamma C_v/(k_B T) \text{[10^{-6} K^{-1}]}$
$C_v/(Nk_b) \text{ is isochoric heat capacities}$
$C_p/(Nk_b) = [C_v/(Nk_b)](1 + \gamma \alpha_p T)$
$g(k_b) = f_s/k_b + P \cdot v(k_b) [K]$
$s$ is the specific entropy
$\Theta'(P) = (\partial \Theta)/(\partial P)_T [\text{K/GPa}]$ $\text{[1]}$
$C_v/(P)/(Nk_b) \text{[10^{-3} GPa]}$ $\text{[1]}$
$\alpha_p(P) = (\partial \alpha_p)/(\partial P)_T [10^{-8} (K-GPa)]$ $\text{[1]}$
$\sigma(P)/(Nk_b) \text{[10^{-3} GPa]}$ $\text{[1]}$
$\sigma(100)/[10^{-3} \text{[J/m}^2]\text{]}$ $\text{[2]}$
$X_s = \sigma(c/B_2)^{2}$ $\text{[2]}$
$\psi_p$ is the Poisson's ratio $\text{[2]}$
$\sigma(T)' = (\partial \sigma)/(\partial T)_P [10^{-6} \text{[J/(m}^2\text{K)}]_T$
$\sigma(T)' = (\partial \sigma)/(\partial T)_P [10^{-6} \text{[J/(m}^2\text{K)}]_T$
$\sigma(T)' = (\partial \sigma)/(\partial T)_P [10^{-6} \text{[J/(m}^2\text{K)}]_T$
$\sigma(P)/(\partial C)/(\partial P)/(\partial T)$ $\text{[2]}$
$\sigma(P)/(\partial C)/(\partial P)/(\partial T)$ $\text{[2]}$

1) Calculated by numerical differentiation of the parameter with respect to pressure along the isotherm.
2) The parameter is calculated at the interatomic plastic potential, i.e. with $D_0$.

When $P = 0$ in the experiments with a macrocrystal, the coefficient of thermal expansion can be measured most accurately. The experimental data for low and high temperatures found in the literature are quite diverse. The measurement error of $\alpha_p$ for germanium according to [21] is 5% at 100 K and 8% at 1000 K. At $T = 100 \text{K}$, the following were obtained: $\alpha_p/[10^{-6} \text{[1/K]}] = 6.88$ [21]; 6.87 [29]; 6.6 [37]; 6.849 [38]. At $T = 1000 \text{K}$, the scatter is more noticeable: $\alpha_p/[10^{-6} \text{[1/K]}] = 22.7$ [21]; 25.38 [29]; 25.53 [37]; 22.077 [38]. These data and the results of our calculations (tables 2 and 4) indicate that the accuracy of calculation of $\alpha_p$ at 100 K using this method is + 4%, and at 1000 K it is – 12%. This can be explained by the fact that our calculation method does not take into account the vacancies, which at
high temperatures and \( P = 0 \) make a significant contribution.

### Table 3. The calculated properties of Ge (listed in Column 1) at \( T = 300 \, \text{K} \).

| Property [unit] | Macro \( N = \infty \) | Nano \( N = 223 \) (\( N_{\text{p}} = 7, f = 1 \)) |
|-----------------|------------------------|-----------------------------------------------|
| \( v = \nu/N \) | \( R = r_{c}c = 1 \) | \( P = 0 \) \( X(N, R=1)/X(\infty) \) | \( X(N, P(N)=0)/X(\infty) \) |
| \( \Theta \) the Debye temperature [K] | \( R = 0.6426 \, \text{GPa} \) | \( P = 0.9971 \) | \( P = 0.6281 \, \text{GPa} \) | \( P = 0.9964 \) |
| \( \gamma = - (\partial \ln \Theta/\partial \ln V)_T \) | \( q = (\partial \ln \Theta/\partial \ln V)_T \) | \( 1.06495 \) | \( 1.06497 \) | \( 1.00033 \) | \( 0.99966 \) |
| \( z = - (\partial \ln q/\partial \ln V)_T \) | \( 3.06294 \) | \( 3.03505 \) | \( 0.88291 \) | \( 0.88088 \) | \( 0.99966 \) |
| \( B_T = - V(\partial^2\Theta/\partial V^2)_T \) [GPa] | \( 75.7168 \) | \( 72.9146 \) | \( 0.78176 \) | \( 0.77437 \) | \( 0.00066 \) |
| \( C_p(T) = (\partial B_p/\partial T)p \) | \( 1.25501 \) | \( 1.24684 \) | \( 1.02671 \) | \( 1.02442 \) | \( 1.27268 \) |
| \( \alpha_p = \gamma C_p/(k_B T) \) | \( \alpha_p B_T = (\partial P/\partial T)_T \) | \( 0.9996 \) | \( 0.9964 \) |
| \( g/\kappa_B = \nu/k_B + P \nu/(k_B T) \) | \( 9.41969 \) | \( 9.64171 \) | \( 1.2726 \) | \( 1.2726 \) | \( 0.9996 \) |

\(*\)**Calculated by numerical differentiation of the parameter with respect pressure along the isotherm.

\( ^{2} \)The parameter is calculated at the interatomic potential of plastic type, i.e. with \( D_i \).

As can be seen from the tables 2-4, the properties of germanium change with the decrease in size in different ways. The following parameters change slightly both with isochoric \( R = r_{c}c = 1 \) and isobaric \( P = 0 \) decrease in \( N \): at \( T = 100 \, \text{K} \): \( v, \gamma, z, B_T, \sigma(100), \mu_p \); at \( T = 500 \) and 1000 K: \( v, \gamma, z, B_T, \alpha_p B_T = (\partial P/\partial T)_c, C, \sigma(100), \mu_p \), and at 1000 K also \( s \).

Therefore, for various calculations within the indicated \( P-T-N \)-conditions, the size dependence of these properties can be disregarded, and the values of the parameters obtained for a macrocrystal can be used when calculating the properties of a nanocrystal. But if the \( P-T-N \)-conditions are different, then the size changes in these parameters may be already noticeable.

Based on the Lindemann melting criterion for the relative melting point, one can derive the following expression [39]:

\[
T_m^* = \frac{T_m(N)}{T_m(\infty)} = \left[ \frac{X_L(N) \Theta(N) \rho(N)}{X_L(\infty) \Theta(\infty) \rho(\infty)} \right]^2 = \left( \frac{X_L^* \Theta^* \rho^*}{X_L \Theta \rho} \right)^2.
\]

Assuming that the Lindemann parameter \( (X_L) \) does not depend on the size of the nanocrystal, we obtain: \( T_m^* = (\Theta^*)^2(v^*)^{2/3} \). From this and from values of \( \Theta^* \) and \( v^* = v(\infty, f)/(v(N=\infty)) \) presented in Table 4 it follows that \( T_m(N=223, f=1)^* \) = (0.87639)^2 (1.00776)^{2/3} = 0.772. Thus, the function of \( T_m(N)^* \) decreases at isobaric reduction of \( N \) less than the relative elasticity modulus \( B_T^* = 0.76 \).

Let us note that, as we showed in [4, 8, 11] on the basis of the RP-model, when the shape of a
nanocrystal deviates from the most energy-optimal shape (a cube for a RP-model), the size dependences of the properties are enhanced. Therefore, the size changes of the properties presented in the tables 2-4 are the minimally possible for the indicated thermodynamic conditions, since they are calculated for the cubic shape of the nanocrystal with the Gibbs free surface. Growing germanium nanocrystals normally have a rod-like or plate-like shape [40].

Table 4. The calculated properties of Ge (listed in Column 1) at \( T = 1000 \) K.

| Property [unit] | \( R = r/c = 1 \) | \( \) | \( P = 0 \) | \( P = 0.9912 \) | \( X(N, P = 0) = 1.9323 \) GPa | \( R = 0.9886 \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( \gamma = \frac{\partial \ln \Theta}{\partial \ln V} \) | 13.6346 | 14.0032 | 1.00000 | 1.00776 |
| \( \Theta \) is the Debye temperature [K] | 482.222 | 468.937 | 0.88351 | 0.87639 |
| \( \gamma - \frac{\partial \ln \Theta}{\partial \ln V} = \frac{3}{2} \left( 1 - \frac{1}{\Theta} \right) \) | 1.04695 | 1.04703 | 1.00033 | 1.00035 |
| \( \frac{1}{\Theta} \) | 3.06294 | 2.97809 | 0.88291 | 0.87578 |
| \( \frac{1}{\Theta} \) | 1.05304 | 1.05295 | 0.99966 | 0.99966 |
| \( B_T = \left( \frac{\partial B_T}{\partial P} \right)_T \) [GPa] | 76.9109 | 68.5291 | 0.78554 | 0.75992 |
| \( \alpha_p = \gamma C^1 \left( k_B T \right) \left( 10^{-6} \text{ K}^{-1} \right) \) | 18.1931 | 19.8941 | 1.27648 | 1.30938 |
| \( \alpha_p = \gamma C^1 \left( k_B T \right) \left( 10^{-3} \text{ GPa/K} \right) \) | 1.39925 | 1.36332 | 1.00273 | 0.99503 |
| \( C_p(Nk_a) \) is isochoric heat capacities | 2.96751 | 2.96927 | 1.00239 | 1.00239 |
| \( C_p(Nk_a) \) | 3.02403 | 3.03112 | 1.00758 | 1.00873 |
| \( g/k_B = f_0/k_B + P \times k_B T \) | -93388.1 | -96609.0 | 0.78382 | 0.79104 |
| \( s \) is the specific entropy | 6.06740 | 6.15032 | 1.06065 | 1.06378 |
| \( \Theta^1(P) = \left( \frac{\partial \Theta}{\partial \ln T} \right)_V \left( K/GPa \right)^1 \) | 6.56941 | 7.16327 | 1.12436 | 1.15382 |
| \( C_r^1(P)/Nk_a \) \left( 10^{-3} \text{ GPa} \right)^1 \) | -0.86779 | -0.94754 | 1.00020 | 1.02611 |
| \( \alpha_p = \gamma C^1 \left( k_B T \right) \left( 10^{-3} \text{ GPa} \right)^1 \) | -77.8259 | -98.9939 | 1.61074 | 1.72545 |
| \( C_r^1(P)/Nk_a \) \left( 10^{-3} \text{ GPa} \right)^1 \) | -3.30474 | -4.04801 | 1.45156 | 1.56305 |
| \( \sigma(100) \left( 10^{-3} \text{ J/m}^2 \right)^2 \) | 121.540 | 122.876 | 0.99030 | 0.98491 |
| \( \sigma(n) \) | 0.13438 | 0.14643 | 1.25175 | 1.28159 |
| \( \mu_\theta \) is the Poisson’s ratio 2) | 0.35820 | 0.36989 | 1.07993 | 1.07756 |
| \( \sigma(T) \left( 10^{-6} \text{ J/m}^2 \text{ K} \right) \) | -42.7250 | -41.9886 | 1.28405 | 1.27747 |
| \( \sigma(T) \left( 10^{-6} \text{ J/m}^2 \text{ K} \right) \) | -73.5613 | -76.7523 | 1.27138 | 1.28577 |
| \( \sigma(P) \left( 10^{-6} \text{ J/m}^2 \text{ GPa} \right)^2 \) | 21.9350 | 25.3895 | 1.25179 | 1.30361 |

1) Calculated by numerical differentiation of the parameter with respect pressure along the isotherm.
2) The parameter is calculated at the interatomic potential of plastic type, i.e. with \( \bar{D}_c \).

5. Conclusion

The change of the state equation affected by a change in the size of germanium nanocrystal at \( T = 100, 300 \) and \( 1000 \) K was investigated. It was shown that at a certain value of the relative volume \( (v/v_0) \), the isothermal dependences of \( P(v/v_0) \) for the nanocrystal and macrocrystal intersect.

At the intersection point (i.e., at \( (v/v_0) \)), the surface pressure becomes equal to zero: \( P_s(v/v_0) = P(Macro) - P(Nano) = 0 \). The value of \( (v/v_0) \) decreases both with an isomorphic-isomorphic rise in temperature, and with an isomorphic-isothermal decrease of \( N \), or with an isomorphic-isothermal deviation of the nanocrystal shape from the energy-optimal shape (a cube for the RP-model).

It was shown that with an isobaric \( (P = 0) \) decrease in size, the specific volume of the germanium nanocrystal increases the more, the higher the temperature of the nanocrystal is. This conclusion is consistent with the experimental results obtained by M.Ya. Gamarnik [17, 18].

Based on the obtained equation of state, the changes in the 23 properties of germanium were studied both at an isochoric \( (R = r/c = 1) \) and at an isobaric \( (P = 0) \) decrease of \( N \). It was shown that during the isobaric \( (P = 0) \) transition from macro- to nanocrystal, the following properties decrease:
at $T = 100$ and $300$ K: $\Theta, q, z, B_T, \sigma \gamma, \sigma(100)$; at $T = 1000$ K: $\Theta, q, z, B_T, \alpha_p B_T, g \sigma(100)$, as well as and the value of $T_m$.

At the same time, the values of the following parameters change

- at $T = 100$ K: $v, \gamma, B'(P), \alpha_p B_T = (\partial \sigma/\partial T)_v, C_v, C_p, s, \Theta(P), C'_v(P), C'_p(P), X_{sc}$
- at $T = 300$ K: $v, \gamma, B'(P), \alpha_p B_T = (\partial \sigma/\partial T)_v, C_v, C_p, s, \Theta(P), C'_v(P), C'_p(P), X_{sc}$
- at $T = 1000$ K: $v, \gamma, B'(P), \alpha_p C_v, C_p, s, \Theta(P), C'_v(P), C'_p(P), X_{sc}$

At the same time, when passing from macro- to nanocrystal, the following parameters change slightly: at $T = 100$ K: $v, \gamma, z, B'(P), \sigma(100), \mu_p$; at $T = 300$ and $1000$ K: $v, \gamma, z, B'(P), \alpha_p B_T = (\partial \sigma/\partial T)_v, C_v, C_p, s, \Theta(P), C'_v(P), C'_p(P), \sigma(100)$, $\mu_p$, and at $1000$ K also $s$. Therefore, for the calculations within these $P-T-N$-conditions, the dimensional dependence of these parameters can be disregarded, and the values obtained for a macrocrystal can be used.

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