On the polymorphism of silicon and germanium

M N Magomedov
Chief Researcher, Institute for Geothermal Problems of Dagestan Scientific Center of Russian Academy of Sciences, Makhachkala, Russia
E-mail: mahmag4@mail.ru

Abstract. Based on the pairwise interatomic Mi-Lennard-Jones potential the state equations and the baric dependencies of the properties for various polymorphic modifications of silicon and germanium were obtained. It is shown that for the semiconductor phase the best results are obtained using the interatomic potential of the elastic type, and for metallic phases the best results are obtained using the potential of the plastic type that has smaller depth of the potential well.

It is known [1-5] that under compression of the silicon (Si) or germanium (Ge) a phase transition (PT) of the first kind is observed, in which a diamond structure (cd-phase) converted in a body-centered tetragonal structure type β-Sn (tin-phase). At this the interatomic bonds are converted from the covalent type to the metal ones. At further compression, the structure of β-Sn is converted in other more dense polymorphs. Although there are many theoretical methods for calculation of equations of state of various crystalline modifications of Si and Ge were proposed [3-5], but the nature of the baric metallization is not entirely clear. Especially unclear the nature of irreversibility of PT from the diamond structure (cd-phase) in the structure β-Sn (tin-phase).

In this paper, the method for calculation of the dependence of pressure (P) versus of volume (V) and temperature (T) of the crystal is proposed, and on the basis of this method the irreversibility of polymorphic PT of the first kind that occur in Si and Ge under compression is studied.

It was assumed that the atoms interact via the pairwise potential of the Mie-Lennard-Jones:

$$\varphi(r) = \frac{D}{(b-a)} \left[ a \left( \frac{r_o}{r} \right)^b - b \left( \frac{r_o}{r} \right)^a \right].$$

(1)

Here, D and r_o are the depth and the coordinate of the potential minimum, b > a > 1 are the numerical parameters.

At normal conditions (T = 300 K and P = 0) the crystals of Si and Ge have the diamond structure (cd-phase) with k_n = 4 and k_p = 0.3401, where k_n is the first coordination number, k_p is the structure packing coefficient. The values of r_o, b and a for cd-phase of Si and Ge were determined in [6], and presented in the table. With regard to D in [6] it was shown that for covalent crystals the value D can be defined both from the elastic modulus (B_0) and from the specific energy of atomization (L_0) at T = 0 K and P = 0 by the equations:

$$D_b = \frac{18B_0 V_0}{k_n a b N} = D_s + \Delta D,$$

$$D_s = \frac{L_0}{k_n/2}.$$  

(2)

For metals these two formulas give the same result, but for the covalent crystals the depth of interatomic potential that is restored from the elastic modulus (D_b) is approximately twice bigger than the magnitude, which follows from the energy of atomization of the crystal (D_s).
Moreover, the difference: \( \Delta D = D_b - D_s \), for crystals of elements of the carbon subgroup (diamond, Si, Ge, \( \alpha \)-Sn, Pb) decreases at increasing of the atomic mass \( m \), and disappears for lead: \( \Delta D(\text{Pb}) \approx 0 \) [6].

**Table.** The parameters of interatomic potential (1) for the diamond structure of Si and Ge.

| Crystal | \( r_0 \) [6] nm | \( b \) | \( a \) | \( B_0 \) [6] GPa | \( D_b \) eV | \( L_0 \) [6] eV | \( D_s \) eV | \( \Delta D \) eV |
|---------|------------------|--------|------|-----------------|---------|----------|---------|---------|
| Si      | 0.2351           | 4.0    | 2.48 | 97.7            | 5.54    | 4.64     | 2.32    | 3.22    |
| Ge      | 0.2450           | 4.3    | 2.75 | 74.9            | 4.03    | 3.88     | 1.94    | 2.09    |

The feature of this interatomic bond is that for its destruction is enough to break the weakest of the two links. It was shown [6, 7] that the energy of whole interatomic bond (\( D_b \)) is working under the elastic (reversible) deformation, and the energy of weak bond (\( D_s \)) is working at the plastic (irreversible) deformation of the covalent crystal. From \( D_b \) it is necessary to calculate parameters that not lead to the interatomic bonds rupture while measurement: the sound velocity, the Debye temperature, the thermal expansion coefficient. From \( D_s \) are calculated parameters, associated with the bonds ruptures, such as energies of sublimation, vacancy formation, self-diffusion and the surface energy. Under the plastic (irreversible) deformation of the covalent crystal only weak links are breaking, and the depth of the potential (1) is determined by the value \( D_s \).

When the parameters of potential (1) were defined, we used the proposed in [8] method for the calculating of the pressure \( P \) versus the volume \( V \) dependence for Si and Ge by means of elastic (i.e. with \( D_b \)) and plastic (i.e. with \( D_s \)) types of potential (1).

![Graph](image)

**Figure 1.** State equation \( P(V/V_0) \) for \( cd \)-phase of silicon (left) and germanium (right).

In Fig. 1 left shows the dependence of \( P(V/V_0) \) for \( cd \)-phase of Si, where \( V_0 = \frac{4}{3} \pi r_0^3/(6 k_p) \). Symbols are the experimental data from [5]: points are Bridgman data, stars are X-ray data. Curve 2 was calculated by means of the Murnaghan–Birch equation in the following form:
\[ P(x) = 1.5B_0 \left( \frac{1-x^2}{x^7} \right) \left[ 1 + \frac{3}{4} (B_0 - 4) \left( \frac{1-x^2}{x^2} \right) \right], \quad x = \left( \frac{V}{V_0} \right)^{1/3}. \] (3)

Curve 3 is the result of calculations by means of the Kwon–Kim equation, which is given by [5]:

\[ P(V/V_0) = B_0 \left[ 1 - (V/V_0) \right]. \] (4)

In Eqs. (3) and (4) for cd-phase of Si there were taken \( B_0 = 97.8 \) GPa and \( B_0' = 4.1 \) [5].

In Fig. 1 right shows the dependencies of \( P(V/V_0) \) for the cd-phase of Ge. Dots and stars are the results of measurements [1] by the methods of ungasketed cell and gasketed cell, respectively. Curve 2 is obtained by the Eq. (3), curve 3 was calculated by the Kwon–Kim equation (4). In Eqs. (3) and (4) for cd-phase of Ge were taken \( B_0 = 74.9 \) GPa, \( B_0' = 4.35 \) [1].

Our calculations at 300 K are shown by curves 1 and 4 for elastic and plastic types of the potential (1), respectively. As it is seen from Fig. 1, our dependencies \( P(V/V_0) \) with the elastic type of the potential (i.e. with \( D_b \) – curve 1) describe well the experimental data for the cd-phase of Si and Ge. Along with this, the calculations with the plastic type of the potential (i.e. with \( D_s \) – curve 4) are yield the values of pressure much less than the experimental data.

It was found that the dependence of \( P(V) \) for the metallized phases of Si and Ge can also be calculated by the method [8], but with the parameters of interatomic potential of the plastic type (i.e. with \( D_s \)). Herewith the values \( r_0 \) i.e. the coordinates of the minimum of potential (1) for \( \beta \)-Sn and HCP structures were determined by means of the known dependence of interatomic distance from the crystal structure [9, p. 141]: if at the polymorphic transformation the value of first coordination number \( k_n \) increases in the sequence:

3 (structure A9) → 4 (A5) → 6 (A5) → 8 (A2) → 12 (A1),

then the length of interatomic bond increases in the sequence:

1.00 → 1.02 → 1.09 → 1.11 → 1.14.

For structures \( \beta \)-Sn and HCP the first coordination number and the packing coefficient are equal [9, p. 167]: \( k_n = 6, k_p = 0.524 \) and \( k_n = 12, k_p = 0.7405 \), respectively. Then for the coordinates of the interatomic potential minimum we can obtained folowing values:

\[ r_0(k_n=6) = 0.25123 \text{ nm} \quad \text{and} \quad r_0(k_n=12) = 0.26276 \text{ nm} \quad \text{for Si}, \]
\[ r_0(k_n=6) = 0.26181 \text{ nm} \quad \text{and} \quad r_0(k_n=12) = 0.27382 \text{ nm} \quad \text{for Ge}. \] (5) (6)

![Figure 2](image-url)  
Figure 2. State equation \( P(V) \) for silicon (left) and germanium (right).
In Fig. 2 shows the dependence $P(V)$ for different structures of Si and Ge. Horizontal lines show the pressure boundary for the polymorphic phases [3, Tabl. 1].

For silicon are obtained (the pressure of the phase transition $P_c$ is given in [GPa]):

$cd \rightarrow (11.7) \rightarrow \beta\text{-Sn} \rightarrow (13.2) \rightarrow Imma \rightarrow (15.4) \rightarrow sh \rightarrow (~38) \rightarrow Cmca \rightarrow (~42) \rightarrow hcp \rightarrow (79-80) \rightarrow fcc$

For germanium are obtained the following estimates for $P_c$:

$cd \rightarrow (10.6) \rightarrow \beta\text{-Sn} \rightarrow (~75) \rightarrow Imma \rightarrow (~85) \rightarrow sh \rightarrow (~100) \rightarrow Cmca \rightarrow (~170) \rightarrow hcp$

Curves show our calculations of $P(V)$ along the isotherm 300 K. 1 and 2 are the state equations for $cd$-phase, which are obtained by means of the elastic and the plastic types of potential (see Fig. 1); 3 and 4 are the state equations for the structure of $\beta$-Sn ($itn$-phase) and for the hexagonal closely packed (HCP) structure, which were calculated with the plastic type of potential (i.e. with $D_s$). The points are the experimental dates from works [1-5].

As can be seen from Fig. 2, the obtained dependencies for Si are in good agreement with experimental data from [2], and for Ge from [1, 4]. The 300 K isotherms calculations for structures $\beta$-Sn and the HCP with the elastic type of potential show that calculated dependence of $P(V)$ lies much higher than the experimental data.

The transition from $D_t$ to $D_h$ indicates that baric metallization of Si and Ge is the same irreversible process, as the plastic deformation of the crystal. For this reason, after removing of the pressure the metallizing state is not returned to the original covalent $cd$-phase, and for the obtaining of the covalent diamond structure from the baric metallized state it is necessary to anneal it under $P = 0$ and at high (500 – 900 K) temperatures [1-3].

By the method presented in [8], the baric dependencies of the lattice properties for the $cd$- and $tin$-phases of silicon and germanium were calculated. The following properties were calculated: $\Theta$ is the Debye temperature and $\Theta'(P) = (\partial\Theta / \partial P)_T$ is the derivative of $\Theta$ with respect to pressure along an isotherm, the first ($\gamma = [\partial \ln(\Theta) / \partial \ln(V)]_T$, the second ($q = [\partial \ln(q) / \partial \ln(V)]_T$) and the third ($z = [\partial \ln(z) / \partial \ln(V)]_T$) Gruneisen parameters. $B_T = - [\partial P / \partial V(T)]_T$ is the isothermal bulk modulus and its pressure derivative $B'(P) = (\partial B_T / \partial P)_T$, $\alpha_p = [\partial \ln(V)/\partial \ln(T)]_P$ is the thermal expansion coefficient and $\alpha_p'(P) = (\partial \alpha_p / \partial P)_T$, $C_v = \alpha_p B_T V T$ and $C_p = C_v (1 + \gamma \alpha_p T)$ are the isochoric and isobaric heat capacity, $C_v'(P) = (\partial C_v / \partial P)_T$ and $C_p'(P) = (\partial C_p / \partial P)_T$, the product: $\alpha_p B_T = (\partial P / \partial V) = (\partial S / \partial T) V$, $\sigma$ is the specific (per unit area) the surface energy for the face (100), and also $\sigma'(T) = (\partial \sigma / \partial T)V$ and $\sigma'(P) = (\partial \sigma / \partial P)_T$.

From the calculation of the isotherm 300 K it follows that at $cd\text{-}tin$ PT the next properties are abruptly increased: $q$, $z$, $\alpha_p$, $C_v$, $C_p$, $\alpha_p'(P)$, $\alpha_p B_T$, and the next ones abruptly reduced: $\Theta$, $\gamma$, $B_T$, $B'(P)$, $|C_v'(P)|$. At $cd\text{-}tin$ PT the thermal expansion coefficient undergoes the greatest change: 80.9 % for Si, and 42.7 % for Ge.

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