Transition pressures and enthalpy barriers for the cd → β-tin transition in Si and Ge under non-hydrostatic conditions

Katalin Gaál-Nagy and Dieter Strauch

Institut für theoretische Physik, Universität Regensburg, D-93040 Regensburg, Germany

(Dated: November 12, 2018)

We present an ab-initio study of the phase transition cd → β-tin in Si and Ge under hydrostatic and non-hydrostatic pressure. For this purpose we have developed a new method to calculate the influence of non-hydrostatic pressure components not only on the transition pressure but also on the enthalpy barriers between the phases. We find good agreement with available experimental and other theoretical data. The calculations have been performed using the plane-wave pseudopotential approach to the density-functional theory within the local-density and the generalized-gradient approximation implemented in VASP.

PACS numbers: 64.70.Kb 71.15.Nc 81.40.Vw

I. INTRODUCTION

The phase transitions in silicon (Si) and germanium (Ge) from the cd phase (cubic-diamond structure) to the β-tin phase (body-centered tetragonal structure, bct) are two of the most studied solid-solid phase transitions in condensed matter physics, both, experimentally and theoretically. In the experiment, the phase transition in Si occurs at around 110 kbar and in Ge at around 105 kbar, where also lower values of the transition pressure are obtained. These lower values are often considered as caused by non-hydrostatic conditions, which are able to reduce the transition pressure.\(^5\)

In fact, the pressure in the anvil cell is not exactly hydrostatic. Usually at pressures up to 100 kbar the pressure-transmitting medium yields nearly hydrostatic conditions.\(^6\) Above 150 kbar a non-hydrostatic pressure profile is visible, and at very high pressures the pressure-transmitting medium becomes solid which causes a strong non-hydrostatic effect. Even in the hydrostatic pressure regime there is a small pressure gradient.\(^7\) Non-hydrostatic pressure profiles can also be an effect of the geometry of the cell.\(^8\) Because of relaxation phenomena which happen in the pressure-transmitting medium the time for compressing and decompressing has an influence on the measurement.

In theoretical investigations generally hydrostatic conditions are assumed. Within calculations using the local-density approximation (LDA) the calculated transition pressures vary between 70 and 99 kbar for Si and between 73 and 98 kbar for Ge. Usually the transition pressure is strongly underestimated by LDA calculations whereas calculations using generalized-gradient approximation (GGA) match the experimental value better (102–104 kbar for Si and 96–118 kbar for Ge). In any case, the discrepancy between experimental and theoretical results can also be due to non-hydrostatic pressure conditions in the experiment. Ab-initio calculations considering non-hydrostatic pressure are rare\(^3\) and deal just with the transition pressure. The influence of non-hydrostatic conditions on the enthalpy barrier between the two phases is not studied within an ab-initio calculation until now. Therefore, we developed a new method to calculate the transition pressure as well as the enthalpy barriers also for non-hydrostatic conditions. In a first step, we obtain the transition pressure and the enthalpy barrier between both phases as a function of pressure starting from a complete numerical equation of state for hydrostatic conditions. Here a complete equation of state means a continuous, multivalued function \(V(p)\) where \(V\) is the volume and \(p\) the pressure, similar to the one of the common textbook example of the van der Waals gas. In a second step, this procedure is extended to non-hydrostatic conditions.

This contribution is organized as follows: Firstly, a short introduction into the theoretical background of the calculations and the properties of the unit cell used for our calculations is given (Section II). Then we explain the procedure of calculating a complete equation of state from a given energy surface (Section III). Following this, we present results for the influence of non-hydrostatic pressure components on the transition pressure and on the height of the enthalpy barrier (Section IV). Finally, after a discussion of the results and comparison with available theoretical data (Section V) we describe possible extensions of our procedure and summarize (Section VI).

II. METHOD

We have carried out calculations with the Vienna ab-initio simulation package (VASP).\(^55,56,57,58\) It is based on one plane-wave pseudopotential approach to the density-functional theory (DFT).\(^59,60\) We have used ultrasoft Vanderbilt-type pseudopotentials\(^61\) as supplied by Kresse and Hafner.\(^62\) The exchange-correlation potential has been calculated within the GGA due to Perdew and Wang\(^63\) for Si and Ge and the LDA\(^64,65\) for Si only. The forces on the atoms are derived from a generalized form of the Hellmann-Feynman theorem\(^67\) including Pulay forces.\(^68\) For the ultrasoft pseudo-
tentials a kinetic-energy cutoff of 270 eV (410 eV) for Si (Ge) has been sufficient for convergence of the total energy and provides an error smaller than 0.5 kbar (0.2 kbar) for Si (Ge) to the pressure according to the Pulay stress. The special-point summation required a $18 \times 18 \times 18$ (24 $\times$ 24 $\times$ 24) mesh of Monkhorst-Pack points which amounts to 864 (1962) k-points in the irreducible wedge of the Brillouin zone for Si (Ge). Since the $\beta$-tin phase is metallic we have used a Methfessel-Paxton smearing with a width of 0.2 eV, including the cd phase, since it is not a priori clear whether a given set of volume $V$ and ratio $c/a$ of lattice constants yields a metallic or a semiconducting phase.

In order to minimize an energy offset between the structures it is important to describe the structures of both phases within the same bct cell (lattice constants $a = b \neq c$) with two atoms in the basis at $(0,0,0)$ and $(0,0.5a,0.25c)$. The symmetry of the cd phase requires $c/a = \sqrt{2}$, whereas $c/a$ can vary for the $\beta$-tin phase. Using the bct cell the structure of the cd phase with respect to the conventional face-centered cubic cell is rotated by $45^\circ$ around the $c$-axis. In the following, CD and BCT denote the structure of the cd- and the $\beta$-tin phase using the bct cell.

III. COMPLETE EQUATION OF STATE UNDER HYDROSTATIC CONDITIONS

Neglecting temperature and zero-point motion effects, the phase with the lowest enthalpy $H = E + pV$ is stable. Therefore, the transition pressure $p^t$ for a first-order pressure-induced phase transition from the cd phase to the $\beta$-tin phase can be determined from the crossing of the corresponding enthalpy curves $H^{\text{cd}}(p)$ and $H^{\beta\text{-tin}}(p)$ with $H^{\text{cd}}(p^t) = H^{\beta\text{-tin}}(p^t)$. First-order phase transitions are accompanied by a discontinuity in the volume $\Delta V$ and an overcoming of an enthalpy barrier which is located between the phases and which has a height of $\Delta H$.

Under hydrostatic conditions the pressure is defined as $p = -\partial E / \partial V$. It can also be determined from the stress tensor $\sigma$.

Since the structures here are orthogonal, the off-diagonal components of $\sigma$ vanish, and $\sigma$ has the form

$$
\sigma = \begin{pmatrix}
\sigma_{11} & \sigma_{12} \\
\sigma_{12} & \sigma_{22} \\
\end{pmatrix} = \begin{pmatrix}
-p_x & -p_y \\
-p_y & -p_z \\
\end{pmatrix} .
$$

We are using a tetragonal cell, and thus $p_x = p_y$. Under hydrostatic conditions all three components are equal and correspond to the external pressure $p$,

$$
p_x = p_y = p_z = p .
$$

Under non-hydrostatic conditions the average pressure is defined as

$$
p_0 = \frac{1}{3} (p_x + p_y + p_z) = -\frac{1}{3} \text{tr} \sigma ,
$$

which is again equal to the external pressure in the case of hydrostatic conditions.

We have calculated the total energy as a function of $V$ and $c/a$. The corresponding energy surface $E(V,c/a)$ is shown in Fig. 1 for Si using the GGA (similar results are obtained for Ge within GGA and for Si within LDA). The two local energy minima, according to the two phases, with a saddle in between are visible. The pressure $p_0(V,c/a)$ is obtained from Eq. (1) and Eq. (3) and is included in the figure. Except along the (dotted) hydrostatic line with $p_x = p_z$ the pressure is non-hydrostatic. The local minima are at the crossing of the $p_0 = 0$ and the hydrostatic $p_x = p_z$ lines which defines the equilibrium position. A similar graph can be drawn also for the enthalpy.

Along the hydrostatic line $p_x = p_z$ the structures are in a local equilibrium, meaning the total sum of internal and external forces caused by the pressure is zero. Hence, this condition can be used to extract the total energy $E$, the external pressure $p_0 = p$, and the volume $V$ from Fig. 1 in order to derive a full equation of state $V(p)$. Also $H(p)$ and, furthermore, the values along the line across the saddle are accessible. These curves are shown in Fig. 1. Here, the ideal cd structure ($c/a = \sqrt{2}$) has been reached only within an error of 1% for the lattice parameters. In order to discriminate the enthalpy curves against each other we have reduced them by a linear background. The local stability is in accordance with the fact that the $V(p)$ curves are monotonically decreasing and the $H(p)$-curves are convex. This is in contrast to the textbook example, the van der Waals gas, where the line corresponding to the dotted line of $H(p)$ is concave.
and signals local instability.

![Graph showing volume, reduced enthalpy, and enthalpy barrier as a function of pressure for Si within GGA.](image)

**FIG. 2:** Volume $V$, reduced enthalpy (see text), and enthalpy barrier $\Delta H$ as a function of the hydrostatic pressure for Si within GGA. The crossing of the solid and the dashed line determine the transition pressure.

The transition pressure $p^t$ obtained from the crossing of the enthalpy curves are listed in Table I. The corresponding change $\Delta V$ in the volume at the phase transition can be read from the upper panel of Fig. 2 as the difference between $V^{\beta\text{-}tin}(p^t)$ (solid line) and $V^{\beta\text{-}tin}(p^d)$ (dashed line). Analogously the enthalpy barrier $\Delta H$ can be determined from the figures. In order to check the reliability of this method we compare the results with our previous ones based on the same total-energy calculations but obtained with a different method to evaluate the transitions pressures and enthalpy barriers. The agreement is very good, and the small differences are due to numerical errors. Thus, we can trust in the new method developed here.

**TABLE I:** Transition pressures $p^t$, volume changes $\Delta V$, and enthalpy barriers $\Delta H$ derived from the complete equation of state in comparison with our previous results obtained with an alternative method (in parenthesis).

|          | Ge-GGA | Si-GGA | Si-LDA |
|----------|--------|--------|--------|
| $p^t$ (kbar) | 96 (96) | 122 (121) | 80 (79) |
| $\Delta V$ ($Å^3$) | 7.5 (7.5) | 8.3 (8.3) | 8.5 (8.5) |
| $\Delta H$ (meV) | 421 (423) | 510 (515) | 502 (508) |

Since we have determined a complete equation of state, we can calculate also the enthalpy barrier as a function of pressure. We have to distinguish between the barrier for the $\beta\text{-}tin \rightarrow \text{cd}$ transition, approaching from the $\beta\text{-}tin$ phase, and the one for the $\text{cd} \rightarrow \beta\text{-}tin$ transition, approaching from the $\beta\text{-}tin$ phase. In general, the enthalpy barrier $\Delta H$ has its origin in the energy saddle between the two phases and can be calculated as the difference of the reduced enthalpy of the phases (solid and dashed lines, respectively) and the one from the saddle (dotted line), see Fig. 2. In particular, the enthalpy barrier from the $\beta\text{-}tin$ phase is the difference between the solid and the dotted line, and the one from the $\beta\text{-}tin$ phase is the difference between the dashed and the dotted line. At the transition pressure $p^t$ the enthalpy barriers from both phases have the same height. The determination of the enthalpy barrier as a function of pressure is important to estimate the barrier in the case of over- and underpressurizing the medium. Hence, the phase transitions will happen at a pressure different from $p^t$ which results in a different height of the barrier. As expected, the enthalpy barrier from the $\beta\text{-}tin$ phase is decreasing with increasing pressure whereas the one from the $\beta\text{-}tin$ phase decreases with decreasing pressure. At zero pressure there is still an enthalpy barrier left for the $\beta\text{-}tin \rightarrow \text{cd}$ transition. This points at the fact that there is no spontaneous transition $\beta\text{-}tin \rightarrow \text{cd}$. In the experiment the phase transition $\text{cd} \rightarrow \beta\text{-}tin$ is irreversible.

**IV. PHASE TRANSITION UNDER NON-HYDROSTATIC CONDITIONS**

The procedure for determining transition pressures and enthalpy barriers described in the previous section can be extended to the case of non-hydrostatic pressure. Besides the hydrostatic condition $p_x - p_x = 0$ the values for non-hydrostatic pressure components $p_x - p_x = d \neq 0$ (with a fixed value of $d$) can be extracted from the energy surface $E(V, c/a)$ along the corresponding lines of Fig. 2. A first naive trial considering just the total energy $E^{\text{nh}}$ under non-hydrostatic conditions and the corresponding values $p^0_{\text{nh}}$ for the average pressure and $V^{\text{nh}}$ for the volume gives wrong results, e.g., an increase of the transition pressure for $p_z > p_x$ and $p_z < p_x$. This is in contrast to the experimental observations. Thus is is necessary to include strain effects.

Similar to the stress tensor of Eq. (1) the strain tensor $\epsilon$ can be reduced to a diagonal form for orthogonal systems $\mathbb{1}, \mathbb{2}, \mathbb{2}$.

$$
\epsilon = \begin{pmatrix}
\epsilon_{11} & \\
\epsilon_{22} & 0 \\
\epsilon_{33} & 0
\end{pmatrix} = \begin{pmatrix}
\epsilon_x \\
\epsilon_y \\
\epsilon_z
\end{pmatrix}
$$

where $\epsilon_x$, $\epsilon_y$, and $\epsilon_z$ are along the cartesian crystal axes. For small stress and homogeneous strain the components
FIG. 3: Contour plot of the total energy $E(V, c/a)$ (solid lines) for Ge (GGA) with an interval of the contour lines of 0.2 eV. Besides the hydrostatic condition (bold solid line) non-hydrostatic conditions ($p_x - p_z = -15, -10, \ldots, 20$) are shown.

The strain-only contribution to the enthalpy vanishes for the cd phase, that it is linear with the pressure for the $\beta$-tin phase, and that it is non-linear for the contribution along the line across the saddle. This effect is apparent in Fig. 4, where the enthalpy including strain is presented. Since there is no strain effect on the cd phase, the change of the transition pressure is due to the strained $\beta$-tin phase. From Fig. 4 we can find the transition pressures for fixed non-hydrostatic conditions in the same manner as mentioned in the previous section.

FIG. 4: Equation of state $H(p_0)$ for non-hydrostatic conditions as a function of the average pressure $p_0$. The difference $p_z - p_x$ of two neighboring lines is 5 kbar. The black dots mark the transition pressures $p_0^\#$.

FIG. 5: Enthalpy barriers at the average transition pressures $p_0^\#$ and transition pressures (average transition pressure $p_0^\#$ and the corresponding components $p_0^x$ and $p_0^z$) as a function of $p_z - p_x$. The dashed line marks the boundary $p_x = 0$ and $p_z = 0$.

of $\epsilon$ can be derived as

$$\epsilon_{jj} = \frac{x_j' - x_j}{x_j},$$

where $x_j$ is the lattice parameter in the $j$-direction. Here $x_j$ corresponds to the unstrained and $x_j'$ to the strained crystal. Including stress and strain the enthalpy can be written as

$$\tilde{H} = \tilde{E} + \sum_{j=1}^{3} \sigma_{jj} \epsilon_{jj},$$

where $\tilde{H}$ is the enthalpy and $\tilde{E}$ the total energy per volume. The calculation of the enthalpy at non-hydrostatic stress is based on Eq. (6). The numerical realization is described in Appendix A.

It turns out that the strain-only contribution to the enthalpy vanishes for the cd phase, that it is linear with the pressure for the $\beta$-tin phase, and that it is non-linear for the contribution along the line across the saddle. This effect is apparent in Fig. 4, where the enthalpy including strain is presented. Since there is no strain effect on the cd phase, the change of the transition pressure is due to the strained $\beta$-tin phase. From Fig. 4 we can find the transition pressures for fixed non-hydrostatic conditions in the same manner as mentioned in the previous section.

FIG. 6: Enthalpy barriers at the average transition pressures $p_0^\#$ and transition pressures (average transition pressure $p_0^\#$ and the corresponding components $p_0^x$ and $p_0^z$) as a function of $p_z - p_x$. The dashed line marks the boundary $p_x = 0$ and $p_z = 0$.

Besides the non-hydrostatic stress we can consider finally also the case of over- and under-pressurization of the crystal. To this end calculations of the enthalpy barriers as a function of the average pressure and non-hydrostatic conditions have been carried out. At very high pressures and very large non-hydrostatic compo-
that they have used different cells for the phases and also to ones including orthorhombic structures, the enthalpy barrier is never smaller than 25 meV for the \( \beta \)-tin \( \rightarrow \) cd transition even at the largest non-hydrostatic conditions. In their molecular-dynamics investigation for Si and Ge, the \( \beta \)-tin \( \rightarrow \) cd transition pressures are slightly different from our results (95.9 kbar for Ge(GGA), 122.1 kbar for Si(GGA), and 39 kbar for Si(LDA)). Although the last values have been obtained also with VASP using GGA, the results agree very well with the ones of Refs. 53 and 54. The difference of the additive constants rely on the different values of the transition pressures in the hydrostatic case. Since Cheng et al.\(^{53,54}\) restricted themselves to the enthalpy difference between the phases using path integrals, the enthalpy barrier was not accessible to them.

The experimental values for the transition pressures vary between 103 and 133 kbar for Si\(^{1,2,3,4,5,6,7}\) and between 103 and 110 kbar for Ge\(^{8,9,10,11}\) where the fitted values are at around 110 kbar and 105 kbar, respectively. In both cases, our results obtained with GGA agree perfectly, whereas the LDA result underestimates the experimental value, which is a well known problem.

The good agreement of our results with the ones of Cheng et al.\(^{53,54}\) confirm the reliability of our method, which provides a larger field of applications. In addition, our method can be extended to, e.g., the \( \beta \)-tin \( \rightarrow \) Imma\( \rightarrow \) sh transitions in Si and Ge. After the extraction of a two-dimensional energy surface from a threedimensional one using the values along the lines where two components of the stress tensor are equal (like in our previous work\(^{16,24}\)), the method mentioned here can be applied to this extracted surface. By the choice of two equal components the main pressure direction is chosen. Further extensions even to non-orthorhombic structures are possible, too.

\section{V. DISCUSSION OF THE RESULTS}

In the past, non-hydrostatic conditions have been investigated for different reasons\(^{53,54,73,74,75,76,77}\). Directly comparable with our results are just the ones from Lee \textit{et al.}\(^{24}\) and Cheng \textit{et al.}\(^{53,54}\). Besides the transition pressures also the function \( p_x^t(p_y^t) \) is given in these contributions. This function can be obtained from our results by a linear fit of the values for the transition pressure in Fig. 6. Already Lee \textit{et al.}\(^{24}\) found a linear relation of \( p_x^t \) and \( p_y^t \). In their molecular-dynamics investigation they found \( p_x^t = 127 \) kbar for hydrostatic conditions and \( p_y^t = p_x^t + 90 \) kbar. The additive constant corresponds to the lowest possible transition pressure. On the contrary, Cheng \textit{et al.}\(^{53,54}\) obtained \( p_x^t = 95 \) kbar and \( p_y^t = 0.737 \) kbar for Ge, and \( p_x^t = 114 \) kbar and \( p_y^t = 0.658 \) kbar for Si. Although the last values have been obtained also with VASP using GGA, the results for the transition pressure are slightly different from our results (95.9 kbar for Ge(GGA), 122.1 kbar for Si(GGA), and 79.6 kbar for Si(LDA)). This can be due to the fact that they have used different cells for the phases and also different pseudopotentials and convergence parameters. The choice of different unit cells can lead to an energy offset between the energy curves to which the transition pressure is very sensitive. Nevertheless, our results for the linear functions which are \( p_x^t = 0.651 \) kbar for Ge(GGA), \( p_x^t = 0.606 \) kbar for Si(GGA), and \( p_x^t = 0.619 \) kbar for Si(LDA), respectively, agree very well with the ones of Refs. 53 and 54. The difference of the additive constants rely on the different values of the transition pressures in the hydrostatic case. Since Cheng \textit{et al.}\(^{53,54}\) restricted themselves to the enthalpy difference between the phases using path integrals, the enthalpy barrier was not accessible to them.

The experimental values for the transition pressures vary between 103 and 133 kbar for Si\(^{1,2,3,4,5,6,7}\) and between 103 and 110 kbar for Ge\(^{8,9,10,11}\) where the fitted values are at around 110 kbar and 105 kbar, respectively. In both cases, our results obtained with GGA agree perfectly, whereas the LDA result underestimates the experimental value, which is a well known problem.

The good agreement of our results with the ones of Cheng et al.\(^{53,54}\) confirm the reliability of our method, which provides a larger field of applications. In addition, our method can be extended to, e.g., the \( \beta \)-tin \( \rightarrow \) Imma\( \rightarrow \) sh transitions in Si and Ge. After the extraction of a two-dimensional energy surface from a threedimensional one using the values along the lines where two components of the stress tensor are equal (like in our previous work\(^{16,24}\)), the method mentioned here can be applied to this extracted surface. By the choice of two equal components the main pressure direction is chosen. Further extensions even to non-orthorhombic structures are possible, too.

\section{VI. SUMMARY}

We have developed a new method for investigating first-order high-pressure phase transitions which is based on the calculation of a complete equation of state. Besides the transition pressure and the volume change, which are also available with the common-tangent construction, the enthalpy barrier between the phases can be obtained with our method. A comparison with results for Si and Ge from common methods shows the reliability of the new method. Further on, the enthalpy barrier can be determined as a function of the external pressure which makes effects from over- and underpressurizing accessible. An extension of this method allows us also to investigate high-pressure phase transitions under non-hydrostatic conditions, in particular the transition pressure and the enthalpy barrier, which are both decreasing if the pressure component along the \( c \)-axis is larger than the other ones. Our results show an excellent agreement with available experimental and theoretical data. This new method can be extended also to other phase transitions and also to ones including orthorhombic structures, for example, the transitions \( \beta \)-tin \( \rightarrow \) Imma\( \rightarrow \) sh. Thus, we have developed a powerful tool for investigating phase transitions under hydrostatic and non-hydrostatic conditions.
Acknowledgment

Support by the Heinrich Böll Stiftung, Germany, is gratefully acknowledged. This work was funded in part by the EU’s 6th Framework Programme through the NANOQUANTA Network of Excellence (NMP4-CT-2004-500198).

APPENDIX A: CALCULATION OF THE ENTHALPY INCLUDING STRESS

Here we give a short description of the formulae used for the calculation of the enthalpy including stress and strain effects starting from Eq. (6).

\[
dH = dE + (p_x a_x + p_y b_y + p_z c_z) V_0 + \left( \frac{\partial E}{\partial a_x} \frac{\partial a_x}{\partial x} + \frac{\partial E}{\partial b_y} \frac{\partial b_y}{\partial y} + \frac{\partial E}{\partial c_z} \frac{\partial c_z}{\partial z} \right) V_0,
\]

which is equivalent to \(dH = dE + pdV\) in the case of hydrostatic conditions. Since Eq. (3) holds just for small stress, we need to integrate this equation and cannot go directly to the absolute values. The integration is performed using the recursively defined equation

\[
H^i = (E_{nh}^i - E_{nh}^{i-1}) + V^{i-1}(p_0 - p_0^{i-1}) + \sum_{j=x,y,z} \frac{x_j^i - x_j^{i-1}}{x_j^{i-1}} p_j
\]

(A2)

where \(x_j\) are the lattice constants along the three cartesian directions \(x, y,\) and \(z\), and the difference from the previous step \((i-1)\) is calculated along a line \(p_0 - p_0^{i-1} = d\) for fixed non-hydrostatic conditions (see Fig. 3) starting from the equilibrium structure of the \(cd\) phase. \(E_{nh}\) is here the total energy along a line \(p_0 - p_0 = d\). The enthalpy \(H(p)\) under non-hydrostatic conditions corresponds to the calculated points \(H'(p')\). By symmetrizing this equation numerical errors have been reduced.
