Origin of enhanced superconducting transition temperature through structural transformation in CaSi$_2$

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Abstract. Using the first-principles lattice dynamics, we have studied physical origin of enhancement in the superconducting transition temperature $T_c$ of CaSi$_2$ with structural phase transition. Optimization results show that CaSi$_2$ has the AlB$_2$ structure as an optimized structure above 17GPa. The electron-phonon interaction is enhanced, when CaSi$_2$ takes the AlB$_2$ structure compared to phase III. Especially, an $E_{2g}$ Einstein mode and a softened optical $B_{2g}$ mode are important.

At ambient pressure, CaSi$_2$ has a rhombohedral crystal structure (phase I). This layered structure is not a superconductor down to 0.03 K [1]. A high pressure phase with the $\alpha$-ThSi$_2$ tetragonal structure (phase II) is known to be a superconductor of $T_c = 1.58$ K [2]. At the pressure $P \approx 10$ GPa, CaSi$_2$ undergoes a structural phase transition into another trigonal structure (phase III) and $T_c$ raises up to $\sim 3$ K [3]. In this structure, silicon atoms form corrugated honeycomb networks. The space-group symmetry is classified in $P3m1$ with Ca at $1a$ (000) site and Si $2d(1\frac{1}{3}z \simeq 0.4)$ sites[4]. It was theoretically predicted that the trigonal structure transformed to the AlB$_2$-type structure ($z=0.5$) [5] and then the transition was experimentally observed at 15 GPa. At this transition, $z$ increases from $\simeq 0.4$, but the wavy honeycomb networks are not perfectly flat ($z \simeq 0.44$) and the space-group symmetry doesn’t change. In this structure (phase IV), $T_c$ further raises up to around 14 K, which has been the highest record for CaSi$_2$.

MgB$_2$ [6], which has been attracting great interest both in basic science and for industrial applications, but, in contrast, CaSi$_2$ has not been investigated enough in the literature. However, this another superconductor has its own interest and importance. This is because, CaSi$_2$ provides us with a testing ground, on which we can compare several polymorphs, which are superconducting. The structures resemble with each other, but $T_c$ changes its value when the structural phase transition takes place. If we find out a key factor determining the behavior of $T_c$ for the structural deformation, the result would help us to understand this superconducting Zintl-phase compound.

The purpose of the present study is thus to explore nature of the pressure-induced phase transition of CaSi$_2$ using the first-principles calculations. Our simulation tells us that CaSi$_2$ undergoes a structural transformation to the AlB$_2$ structure. This phase is expected to be a
superconductor with much higher $T_c$ than that of the phase III. We will focus on the reason why $T_c$ raises in the higher pressure AlB$_2$ phase of CaSi$_2$.

We treat the phases III, IV and the AlB$_2$ structure in this study. For the determination of the electronic structure, we utilized the density-functional theory calculation [7, 8] in a generalized gradient approximation [10] and an Vanderbilt ultrasoft pseudo potential [9]. The Kohn-Sham wavefunctions and the electronic charge density are expanded in the plane-wave basis. For calcium atoms, 3s, 3p and 4s electrons are treated as the valence electrons, while 3s and 3p levels are in the valence levels for silicon. The energy cutoff for the wave functions is 16 Ry and that for the charge density is 64 Ry. The $k$-space (electron) and $q$-space (phonon) integrations are done using $12\times 12\times 12$ and $4 \times 4 \times 4$ in Monkhorst-Pack grids [11]. We optimized the lattice constants $a, c$ and internal parameter $z$ by Parrinello-Rahman constant-pressure molecular dynamics [12]. $T_c$ is estimated by the strong coupling theory [13, 14], in which the electron-phonon matrix elements as well as the dynamical matrix elements given by the density functional perturbation theory [15]. These calculations are performed by the PWSCF code [16].

The optimized values of lattice constants $a, c$ and internal parameter $z$ are shown in Fig. 1. In the pressure region from 10 to 15 GPa (phase III), the obtained values are close to the experimentally observed values and the relative error is within 2% for $a, c$ and $z$. But, $z$ dramatically increased at 17 GPa and it reached to 0.5, that is to say, the corrugated structure transforms to AlB$_2$ structure. The result is confirmed by the accurate calculation with energy cutoff for wave functions of 40 Ry starting from the structure observed in the experiment.

At the critical pressure, $c$ suddenly decreases but $a$ becomes large for preventing a sudden change of the unit cell volume. Next, $z$ approaches to 0.5 and the silicon plane becomes flat. Thus our result indicates that the silicon network in CaSi$_2$ prefers to have a hexagonal planer structure and the AlB$_2$ structure should appear at the high pressure. Note that, since the value of the pressure given by the first-principles calculation could have an error, the critical pressure may be much higher in the real experiment.

In order to test stability of the AlB$_2$ structure, we investigated phonon dispersions at each phase (Fig. 2). If the lattice is unstable, a phonon mode with an imaginary frequency appears. In the present result, we have always real frequency in the whole Brillouin zone. This result suggests that the AlB$_2$ structure is stable in a pressure range $P> 17$ GPa.

Comparing results for two phases, it is found that one optical phonon mode is softened in the AlB$_2$ structure. Corresponding atomic displacement is the out of plane vibration mode of silicon, in which a Si plane becomes corrugated. Thus the mode is a $B_{2g}$ mode. The softening of the $B_{2g}$ mode is reasonable, since the AlB$_2$ system should be unstable against corrugation in Si planes by reducing the pressure. Another characteristic feature of this AlB$_2$ structure is appearance of a flat phonon dispersion at the highest energy branch. This suggests that the highest optical $E_{2g}$ mode, which is an in-plane longitudinal motion of Si atoms, is an Einstein mode.

We determine which phonon mode has the largest electron-phonon interaction. We estimate partial electron-phonon interaction parameter $\lambda_{\nu}(q)$, which represents interaction between electron and phonon whose mode is $\nu$, wave number is $q$ (usual electron-phonon interaction parameter $\lambda = \sum_{\nu} \lambda_{\nu}(q)$). In Fig. 2, $\lambda_{E_{2g}}$ is plotted by a circle on each phonon band. This figure indicates that, in the AlB$_2$ structure, the highest mode at the $\Gamma$ point is the most effective. This mode is the $E_{2g}$ mode, in which the neighboring silicon atoms oscillate in the anti phase within a plane. In addition, we see another important mode, the softened optical mode around the $\Gamma$ point. This mode is the $B_{2g}$ mode. Due to the softening, $\lambda_{E_{2g}}(q)$ has a large value, which can contribute to the high $T_c$.

Utilizing the strong coupling theory of the superconductivity [13], we estimated $T_c$. Within the formulation of the isotropic Eliashberg formulation [14], $T_c$ is given by three parameters - the electron-phonon interaction parameter $\lambda$, the weighted average of the phonon frequency
ω_{log}, and the screened Coulomb interaction parameter μ^* - as the following.

\[ T_c = \frac{\omega_{log}}{1.2} \exp\left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right) \]  

(1)

Utilizing the estimated values of λ and ω_{log}, we may discuss a pressure dependence of \( T_c \). As for \( \mu^* \), we assume that \( \mu^* \sim 0.1 \) which may hold for simple metals.

The calculated \( T_c \) for the phase III is 0.1 ~ 0.2 K. It’s almost one-tenth of the experimentally observed value ~ 3 K. This discrepancy may be due to utilization of an additional isotropic approximation in the Eliashberg theory, which results in a small value of \( \lambda = 0.27 \). Although the estimation of \( T_c \) contains an error, we are able to consider qualitative difference of the AlB\(_2\) phase from the low-pressure phases.

**Figure 1.** Optimized lattice parameters (a) lattice constant a, (b) lattice constant c, (c) internal parameter z and (d) unit cell volume of CaSi\(_2\) at each pressure. For each panel, the optimized values in the simulation are indicated by open circles, while the experimentally observed values [4] are displayed by closed circles.

**Figure 2.** Phonon dispersions \( \omega_\nu(q) \) and partial electron-phonon interactions \( \lambda_\nu(q) \) of CaSi\(_2\) at pressures of (a) phase III and (b) AlB\(_2\) structure. Circles are proportion to \( \lambda_\nu(q) \).
We next consider the pressure dependence of $T_c$ assuming that the AlB$_2$ structure appears in the high pressure. When the structure becomes the AlB$_2$ structure, $T_c$ raises rapidly and reaches a value one order of magnitude larger than the low pressure phase III. The overall tendency seems to be consistent with the experimental fact, in which the phase IV structure has higher $T_c$ than the phase III. In addition, we can expect the softened $B_{2g}$ mode and the high-frequency $E_{2g}$ Einstein mode in the AlB$_2$ structure.

Let us discuss origin of the pressure dependence of $T_c$ in our theoretical data. As mentioned above, $T_c$ is determined by three parameters, two of which are affected by the structural transformation in the present approach. Through structural phase transition, $\lambda$ increases from 0.27 to 0.41, while $\omega_{\log}$ decreases from 300 K to 280 K. So, $\lambda$ increases by a factor of 1.5 in the AlB$_2$ structure. On the other hand, $\omega_{\log}$ decreases only about 10%. Thus, the increase of $T_c$ is caused by the enhancement in the electron-phonon interaction. Two important modes, $B_{2g}$ and $E_{2g}$, behave in a characteristic manner as follows. The strong coupling with the $E_{2g}$ mode is similar to the case of MgB$_2$. In the present material, electrons in the $\sigma^*$ band contribute to this electron-phonon interaction. At the same time, we have another important branch, the $B_{2g}$ soft mode. The softening around the phase boundary of the structural transformation often contributes to enhance $T_c$. However, the softening may reduce $\omega_{\log}$ and finally $T_c$ as exemplified in iodine [18]. In the present case, we have the high-frequency Einstein mode, whose frequency becomes even higher than the low pressure phase. $\omega_{\log}$ is kept almost at the same order of magnitude. Thus we have a prominent increase in $T_c$ estimated for the AlB$_2$ structure from the value of the Phase III.

First principles calculation showed that AlB$_2$ structure may appear as the high-pressure phase of CaSi$_2$. In the AlB$_2$ structure enhancement of $T_c$ is expected because the electron-phonon interaction increase. The $E_{2g}$ and $B_{2g}$ modes of phonon are effective for the enhanced electron-phonon interaction.

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