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Abstract
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Pressure effects on the superconducting transition in nH-CaAlSi

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We present a combined experimental and theoretical study of the effects of pressure on $T_c$ of the hexagonal layered superconductors $nH$-CaAlSi ($n = 1, 5, 6$), where $nH$ labels the different stacking variants that were recently discovered. Experimentally, the pressure dependence of $T_c$ has been investigated by measuring the magnetic susceptibility of single crystals up to 10 kbar. In contrast to previous results on polycrystalline samples, single crystals with different stacking sequences display different pressure dependences of $T_c$. $1H$-CaAlSi shows a decrease of $T_c$ with pressure, whereas $5H$ and $6H$-CaAlSi exhibit an increase of $T_c$ with pressure. Ab-initio calculations for $1H$, $5H$ and $6H$-CaAlSi reveal that an ultrasoft phonon branch associated to out-of-plane vibrations of the Al-Si layers softens with pressure, leading to a structural instability at high pressures. For $1H$-CaAlSi the softening is not sufficient to cause an increase of $T_c$, which is consistent with the present experiments, but adverse to previous reports. For $5H$ and $6H$ the softening provides the mechanism to understand the observed increase of $T_c$ with pressure. Calculations for hypothetical $2H$ and $3H$ stacking variants reveal qualitative and quantitative differences.

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Superconductivity in hexagonal layered compounds has attracted broad interest since the discovery of “high-$T_c$” superconductivity in MgB$_2$ and other structurally related compounds such as (Ca, Sr)AlSi$_2$ and very recently, alkaline-earth intercalated graphites. In all these compounds the light elements are arranged in honeycomb layers which are intercalated by alkaline earth atoms. Depending on the elements forming the honeycomb layer, the electron and phonon states involved in the superconducting pairing are quite different. In MgB$_2$, holes in the $\sigma$ bands of the B layer couple strongly to B bond-stretching phonon modes. In CaSi$_2$, which can be considered as the “antibonding analogue” to MgB$_2$, the $\sigma^*$ bands are strongly coupled to the bond-stretching phonons of the Si layer. In CaC$_6$ and CaAlSi, the so-called “interlayer” bands are filled and experience significant electron-phonon ($e$-ph) interaction to the out-of-plane buckling vibrations of the honeycomb layers.

CaAlSi is of particular interest because it exhibits an ultrasoft phonon mode and crystallizes with several stacking variants. The interplay of these two ingredients gives rise to intriguing effects both on the normal and the superconducting properties. The presence of an ultrasoft phonon mode at $\sim 7$ meV was initially evidenced by first-principles calculations and recently confirmed by neutron-scattering experiments. The ultrasoft phonon modes are believed to induce strong e- ph coupling and to lead to an enhanced specific heat anomaly at $T_c$ as well as to a positive pressure dependence of $T_c$ in CaAlSi. These effects have not been observed in the isoelectronic and isostructural SrAlSi which does not display any signature of soft phonon modes.

Recent X-ray diffraction experiments on $nH$-CaAlSi single crystals revealed several stacking variations of two different types of Al-Si layers, denoted as A and B in the following (see Fig. 1). The A- and B-layers differ by a rotation around the $c$-axis of $60^\circ$ with respect to each other. Flat and buckled Al-Si layers are indicated with and without an asterisk, respectively.

![Diagram of stacking variants](image)

**FIG. 1:** (color online) Crystal structure of $1H$, $5H$ and $6H$-CaAlSi, which are characterized by a different sequence of A- and B-layers. A- and B-layers are rotated by $60^\circ$ around the $c$-axis with respect to each other. Flat and buckled Al-Si layers are indicated with and without an asterisk, respectively.
unlike neighboring layer. Subsequent investigations show that the superconducting properties strongly depend on the kind of stacking of A- and B-layers.\textsuperscript{14,19,20,21} However, all \textit{ab-initio} calculations, and analyses of the experimental data based thereon, so far have assumed that the stacking of Al-Si planes along the $c$ axis is either uniform, or completely disordered. To clarify the complex interplay of stacking variants, buckling, soft modes and superconductivity, further investigation of the $e$-ph properties of different stacking variants of CaAlSi are highly desirable.

In this paper, we investigate the effects of pressure on the superconducting properties of $nH$-CaAlSi by experiments on single crystals and \textit{ab-initio} calculations of the $e$-ph properties. Previous experiments on polycrystalline samples of CaAlSi and SrAlSi have shown that $T_c$ of CaAlSi increases under pressure while $T_c$ of SrAlSi decreases.\textsuperscript{18} In an \textit{ab-initio} study, Huang et al. have proposed that in 1$H$-CaAlSi an enhancement of the $e$-ph coupling associated to the ultra-soft phonon modes can overcome the negative contribution of the other phonon branches and lead to an increase of $T_c$ under pressure. Such an ultra-soft phonon mode was not obtained for SrAlSi.\textsuperscript{18}

However, recent experimental and theoretical results question these findings. First, until now the pressure dependence of $T_c$ in polycrystalline samples has been interpreted assuming a $1H$ stacking variant. However, we will demonstrate here that the pressure dependence of $T_c$ of 1$H$-CaAlSi single crystals is markedly different from that of polycrystalline samples. Secondly, in these calculations, the soft phonon branch in CaAlSi is unstable in some part of the brillouin zone (BZ), already at ambient pressure. This instability was not confirmed by recent \textit{ab-initio} calculations and neutron scattering experiments.\textsuperscript{12,22} Finally, Huang \textit{et al.} assumed a uniform compressibility, which is very unlikely to occur in layered materials.

The aim of our analysis is two-fold: on the one hand we wish to investigate the interplay between soft modes and superconductivity in 1$H$-CaAlSi based on \textit{ab-initio} calculations and experiments on single crystals. On the other hand, we wish to understand how stacking variants affect the pressure dependence of the superconducting properties of CaAlSi.

Single crystals of CaAlSi were grown by the floating zone method. Details of the crystal growth and characterization are described elsewhere.\textsuperscript{22} The superconducting transition temperature ($T_c$) under pressure was determined by measuring the magnetic susceptibility in a SQUID magnetometer (Quantum Design). A Cu-Be piston-anvil-type pressure cell was used to apply quasi-hydrostatic pressures up to $P \sim 10$ kbar with silicon oil or Fluroinert as pressure transmitting medium. To monitor the pressure inside the pressure cell, we performed \textit{in-situ} measurements of the $T_c$ of Sn (purity 99.999%) or Pb (purity 99.9999 %).\textsuperscript{22}

Figure 2 shows the temperature dependence of the magnetic susceptibility ($\chi(T)$) of single crystals of $nH$-CaAlSi under pressures up to $\sim 10$ kbar. At ambient pressure, the $T_c$’s of 1$H$, 5$H$, and 6$H$-CaAlSi are 6.50 K, 5.95 K, and 7.89 K, respectively, consistent with previous reports.\textsuperscript{14} The superconducting transitions are relatively sharp for 1$H$ and 6$H$-CaAlSi with a transition width of $\Delta T_c \sim 0.1$ K at 80% of the diamagnetic shielding, indicating a good sample quality. For 5$H$-CaAlSi, the transition is broader ($\Delta T_c \sim 0.4$ K), but still sharp enough to follow its pressure dependence. With increasing pressure, the superconducting transition for 1$H$-CaAlSi clearly shifts to lower temperatures without significant broadening of the transition. In contrast, $T_c$ in 5$H$ and 6$H$-CaAlSi increases with pressure. For all samples, the $T_c$’s and the shape of $\chi(T)$ trace taken after gradually releasing again the pressure agreed with the data collected with increasing pressure.

Our measurements reveal that the pressure variation of $T_c$ of $nH$-CaAlSi depends strongly on the stacking sequence. For the detailed comparison, $T_c$ was identified as the temperature where the extrapolation of the steepest slope of $\chi(T)$ intersects the normal-state susceptibility extrapolated to lower temperatures. Using different criteria to determine $T_c$, e.g., the mid-point of the transition, changes the absolute value of $T_c$, but does not alter the relative variation of $T_c$. Surprisingly, for 1$H$-
CaAlSi, $T_c$ decreases linearly with a rate of $\Delta T_c/T_c = -0.03$ K/kbar, in contrast to a previous report on polycrystalline samples.\textsuperscript{12} For $5H$-CaAlSi the pressure dependence is slightly nonlinear with an initial slope of $+0.013$ K/kbar, while $6H$-CaAlSi exhibits a more pronounced nonlinear behavior and saturation at $T_c \sim 7.95$ K already at $\sim 10$ Kbar.

In order to understand the effects of pressure and stacking variants on the superconducting properties of CaAlSi, we performed \textit{ab-initio} (DFPT) calculations\textsuperscript{22-24} of the electronic and vibrational properties of $nH$-CaAlSi as a function of pressure. The computational details are the same as in Ref.\textsuperscript{12} unless otherwise specified.\textsuperscript{25} Besides the identified $1H$, $5H$ and $6H$ stacking variants, we also considered hypothetical $2H$ and $3H$-CaAlSi, characterized by an $|AB\rangle\langle AB|$ and $|AAB\rangle\langle AAB|$ stacking of the Al-Si planes, respectively.

In the investigated pressure range up to 100 kbar, we relaxed the internal parameters of all structures at intervals of 20 kbar. The details of the optimization, together with the detailed band structures and phonon dispersion relations, will be published elsewhere. We subsequently fitted the $E$ vs. $V$ curves to a Birch-Murnaghan equation-of-state, to obtain the equilibrium volume $V_0$ and the bulk modulus $B_0$ for each system. All equilibrium volumes and bulk moduli $B_0$ for each of the identified phases. In sign and magnitude, our calculations correctly reproduce the corrugation (“buckling”) of the Al-Si planes in the $5H$ and $6H$ structures. A corrugation is also obtained for $3H$-CaAlSi. In contrast to previous suggestions,\textsuperscript{12} the corrugation in the Al-Si layers of the $5H$ and $6H$ phases is not reduced by applying pressure. Rather, it remains unchanged for $6H$, or becomes even more pronounced for $5H$-CaAlSi. The compressibility is anisotropic, $k_c/k_a = 3.8$, as expected for a layered material. At all pressures, the total energy of $2H$-CaAlSi and $3H$-CaAlSi is higher than in $1H$, $5H$ and $6H$-CaAlSi, the latter being almost degenerate in energy.\textsuperscript{26}

Using the relaxed structures, we calculated by linear response the phonon dispersion relations $\omega_{q,v}$ and the $e$-phonon linewidths $\gamma_{q,v}$ on a regular grid in $q$-space. The phonon dispersions and the phonon Densities of States (phDOS) were then obtained by Fourier interpolation of the dynamical matrices, while the Eliashberg spectral functions $\alpha^2 F(\omega)$ and the total $e$-phonon coupling $\lambda$’s were calculated by summing over individual linewidths and frequencies.

In Fig. 3 we display the phDOS of $nH$-CaAlSi, calculated at the theoretical equilibrium pressure ($P = 0$) and at the highest pressure considered (100 Kbar). At $P = 0$, the $1H$, $5H$ and $6H$ stacking variants all show a peak at $\sim 7$ meV, associated with the out-of-plane vibrations of the Al-Si planes. Under pressure, roughly one half of the corresponding phonon states soften and drive the system to a structural instability at $P \sim 80$ Kbar.\textsuperscript{27} The hypothetical $2H$-CaAlSi and $3H$-CaAlSi, on the other hand, do not display the ultra-soft phonon peak at $P = 0$, and all phonon modes harden with increasing pressure.

At present, we cannot conclusively explain the different phonon softening behavior of the systems. However, by comparing our (partial) phDOS’s obtained for different $nH$ stacking variants with those of previous VCA calculations\textsuperscript{13,16} we observe that phonon softening mainly involves Al out-of-plane vibrations. Phonon softening appears if a block of three or more like planes is found in the sequence. This probably reflects the tendency of Al to form bonds with other Al atoms in the neighbouring layers rather than $sp^2$ bonds with Si in the same layer, if the $c$ lattice constant is small enough.

Our results strongly differ from those of Ref.\textsuperscript{10} for $1H$-CaAlSi. At $P = 0$, our phonon frequencies are all real, and even at higher pressures only a few become imaginary, while in Ref.\textsuperscript{10} the whole out-of-plane branch becomes unstable. The most likely reason for this discrepancy is that we optimized the structural parameters, while the previous work assumed an isotropic compressibility. Also, a careful convergence of phonon frequencies with respect to $k$-sampling and basis set size is crucial to obtain the correct behaviour of the ultra-soft phonon modes.

![FIG. 3: (color online) Linear Response Phonon DOS (phDOS) for different $nH$-CaAlSi at $P=0$ and $P=100$ kbar; in the right sub-panel we show an enlargement of the low-energy region.](image)

![FIG. 4: (color online) (a) Pressure dependence of the DOS at $E_F$ and (b) frequency of the lowest-lying phonon branches at the $H$ point for various $nH$-CaAlSi.](image)
If the coupling to the electrons is strong enough to overcome the opposing effect of the hardening of the other phonons and of the decrease of the electronic DOS at the Fermi level, a soft phonon mode can lead to an increase of \( T_c \), with pressure. In Fig. 4 we show the calculated pressure dependences of the electronic DOS at the Fermi level, \( N(E_F) \), and of the lowest lying phonon frequency at the \( H \) point (\( \omega_H \)) for 1\( H \), 5\( H \), and 6\( H \)-CaAlSi. We estimate the pressure evolution of the partial \( e\)-ph coupling constant associated to the soft phonon mode, using the Hopfield formula: \[ \lambda = N(E_F)P^2/\omega_H^2 \], where \( I \) is the \( e\)-ph matrix element. Assuming that \( I \) is independent of pressure, we estimate that the partial \( \lambda \) increases by \( \sim 60\% \) for 1\( H \) and 6\( H \), and \( \sim 50\% \) for 5\( H \). For 2\( H \) and 3\( H \)-CaAlSi (not shown), \( N(E_F) \) decreases and \( \omega_F \) increases, resulting in a net decrease of \( \lambda \). From this argument, one could expect a very similar (increasing) behavior of \( T_c \) with pressure for \( n = 1, 5, 6 \). This is, however, not observed experimentally.

Figure 5 shows the evolution of the Eliashberg function \( \alpha^2 F(\omega) \) of 1\( H \)-CaAlSi for which we ran a full \( e\)-ph calculation as a function of pressure. In agreement with previous calculations\(^{12,17} \) at \( P = 0 \) there is a large peak at \( \omega \sim 7 \) meV, associated to the Al-Si out-of-plane vibrations in the \( k_z = \pi/c \) plane, implying that the corresponding phonon states have a considerable coupling to electrons. At higher pressures, following the behavior of the phDOS, this peak splits into two peaks, one of them softening, the other hardening with increasing pressure. The pressure-induced transfer of the spectral weight from the hard to the soft part of the low-lying peak affects both the total \( e\)-ph coupling parameter \( \lambda = 2 \int_0^\infty \alpha^2 F(\omega)\omega^{-1}d\omega \) and the logarithmic-averaged phonon frequency \( \langle \omega_m \rangle \).

Using the Allen-Dynes equation\(^{32} \)

\[
T_c = \frac{\langle \omega_m \rangle}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - (1 + 0.62\lambda)\mu^*} \right],
\]

where \( \mu^* \) is the Coulomb pseudopotential, fixed to \( \mu^* = 0.1 \) in the following (see Tab. I), we obtain a decrease of \( T_c \) with pressure for 1\( H \)-CaAlSi, in agreement with our experiments. A slight variation of \( \mu^* \) does not alter this general behavior.

In stark contrast to the previous report for 1\( H \)-CaAlSi,\(^{12,17} \) the effect of softening of the ultra-soft phonon modes is apparently not sufficient to overcome the opposing contributions from the other phonon branches. For further model calculations, we used a decomposition of \( \alpha^2 F(\omega) \) of 1\( H \)-CaAlSi into Gaussians as shown in Fig. 5. Using this decomposition reveals that the behavior of \( T_c \) with pressure follows that of the spectral weight of the ultra-soft phonon mode, which is decreasing with pressure in 1\( H \)-CaAlSi. The change of the spectral weight of the ultra-soft phonon mode determines the behavior of \( T_c \) under pressure, more importantly than the decrease of its phonon frequency.

For 5\( H \) and 6\( H \)-CaAlSi, due to their very large unit cells (15 and 18 atoms, respectively), and the extreme sensitivity of the results to computational parameters, we did not perform a full \( e\)-ph calculation. Although there are some subtle differences in the electron and phonon dispersions, the results shown in Fig. 5 and 4 imply that the pressure dependence is qualitatively very close to that of 1\( H \)-CaAlSi, (i.e. the \( N(E_F) \)'s and \( \omega_H \) decrease with the same rate, and a structural instability happens at elevated pressures). For this reason, we assume that their \( \alpha^2 F(\omega) \)'s have very similar characteristics to that of 1\( H \)-CaAlSi. The different pressure dependence of \( T_c \) for 5\( H \) and 6\( H \) therefore has to be attributed to a different (increasing) behavior of the spectral weight for the ultra-soft phonon mode under pressure. This behavior could reflect either small differences in \( e\)-ph matrix elements due to the buckling of some planes, or a different number of phonon modes that soften under pressure.

Another aspect, which we cannot rule out completely is, that in 5\( H \) or 6\( H \)-CaAlSi multi-band effects become relevant. Recently Lupi et al. reported an anisotropy of the optical response in the superconducting and the normal states for a crystal with mixed 5\( H \) and 6\( H \) phases.\(^{21} \)

The superconducting gap, determined by penetration

\[
\begin{array}{ccc}
 P (\text{Kbar}) & \langle \omega_m \rangle (\text{K}) & \lambda & T_c (\text{K}) \\
 0 & 139.2 (160) & 0.73 (0.60) & 5.35 (3.66) \\
 20 & 139.9 (186) & 0.70 (0.47) & 4.86 (1.75) \\
 40 & 134.0 (200) & 0.70 (0.43) & 4.65 (1.24) \\
\end{array}
\]

TABLE I: Calculated superconducting properties of 1\( H \)-CaAlSi as a function of pressure. \( T_c \) was obtained by Allen-Dynes formula, with \( \mu^* = 0.1 \). For comparison, we give in parentheses the results for 2\( H \).
depth measurements, also shows a sizable anisotropy, depending on the stacking sequences. Further studies are needed to clarify this point. In particular, understanding the effect of buckling of the Al-Si layers on the anisotropy of the e-ph coupling appears to be the crucial issue.

We would like to emphasize once more that the hypothetical systems 2H and 3H-CaAlSi show a completely different behavior. First, they are energetically disfavored with respect to existing stacking variants, because of a non-optimized energy balance between the formation of AB interfaces and buckling. Second, they do not display any soft phonon modes, which only appear if three or more Al atoms arrange in a sequence along the c-axis.

All phonon modes harden with pressure, leading to an increase in $\langle \omega_\alpha \rangle$, a fast decrease of $\lambda$, and a net decrease of $T_c$ with pressure at a rate of $dT_c/dP \sim -0.05$ K/Kbar. For comparison, the results for 2H-CaAlSi are also listed in Table I. 2H and 3H-CaAlSi, therefore, do not represent proper models for other stacking variants.

In summary, we demonstrate that for single crystals of nH-CaAlSi the behavior of $T_c$ under pressure depends crucially on the particular stacking sequence and the buckling of the Al-Si layers. $T_c$ decreases for 1H, and increases with pressure in 5H and 6H-CaAlSi. Previous experiments on polycrystalline samples gave results that are closer to the behavior of 6H-CaAlSi, but adverse to the behavior of 1H-CaAlSi. One may speculate that the polycrystalline sample consisted mainly of phases with stacking variants other than 1H-CaAlSi. Based on our ab-initio calculations we find a gradual softening of an out-of-plane phonon mode under pressure for nH-CaAlSi ($n = 1, 5, 6$), which leads to a structural instability at higher pressures. In 1H-CaAlSi, the softening is not strong enough to lead to an increase in $T_c$, in contrast to previous calculations, while it is likely that this softening leads to the increase of $T_c$ with pressure in single crystals of 5H and 6H-CaAlSi.

Acknowledgments

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2. For a review on recent progress in MgB$_2$ research, see Physica C 456 (2007).
23. In panel (a), to obtain the theoretical $T_c$, we used the Allen-Dynes formula with $\mu^* = 0.072$ in order to match the experimental $T_c$ at $P=0$. The other parameters are in table I. In panel (c), the $T_c$ vs. $P$ curve for polycrystalline samples is obtained from the raw susceptibility data of Ref. 18, using the same criteria for determining $T_c$ that we used for single crystals.
26. X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G.

27 In the present paper, we devoted special care to the convergence of the e-ph coupling functions with pressure, which turned out to depend critically on the q-space integration, particularly along the c direction. For the higher pressures, a 6 × 6 × 12 q-grid was found necessary to ensure convergence.

28 Experimentally-realized (n = 1, 5, 6) stacking variants are those for which the energy cost of creating AB interfaces is compensated by the energy gain due to the buckling of boundary layers.


30 For consistency, we used the theoretical lattice constants at all pressures. At P = 0, the deviation between the theoretical and experimental lattice constant is less than 1%, which has no effect on the calculated phonon frequencies for all systems and on the electronic DOS for 1H and 6H. For 5H, using the experimental lattice constant at P = 0 we obtain a much lower value for \(N(E_F) = 1.1\) st./eV f.u., in perfect agreement with other calculations (Ref. 24), and much closer to that of 1H and 6H.

31 Preliminary X-ray measurements confirm a structural instability for 1H-CaAlSi at \(\sim 9\) GPa; J. S. Kim, X. Wang, K. Syassen, R. K. Kremer, and M. Hanfland (unpublished).