

Pressure effects on the superconducting transition in nH-CaAlSi

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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 $CaSi_2$, 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 different. In MgB_2 , holes in the σ -bands of the B-layer couple strongly to the B bond-stretching phonon modes. In $CaSi_2$, which can be considered as the ‘antibonding analogue’ to MgB_2 , the σ^* -bands are strongly coupled to the bond-stretching phonons of the Si-layer. In alkali-earth intercalated graphites, CaC_6 and SrC_6 , 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 [1].

$CaAlSi$ belongs to a class of recently synthesized ternary alloys, formed by Al and Si atoms sitting on graphene-like sheets, and alkaline-earth atoms (Ca, Sr, Ba) intercalated between them. $CaAlSi$ and $SrAlSi$ are superconducting, with a T_c of 7.8 K and 5.4 K respectively, while $BaAlSi$ is not down to 0.3 K [2]. Like in CaC_6 and SrC_6 , the superconductivity is mainly due to the interaction of ‘interlayer’ and π^* electrons with the out-of-plane vibrations of the honeycomb layers; the σ -bands are completely full and do not contribute to the pairing [3].

$CaAlSi$ has recently attracted considerable interest, because it exhibits an ultrasoft phonon mode and crystallizes with several stacking variants. Thermodynamic experiments on polycrystals have revealed unexpected differences between $CaAlSi$ and the isoelectronic and isostructural $SrAlSi$. Whereas $SrAlSi$ behaves like a standard weak-coupling BCS superconductor, $CaAlSi$ is in the strong-coupling limit. Furthermore, T_c *decreases* with pressure in

$SrAlSi$, and *increases* in $CaAlSi$. *Ab initio* calculations, and later neutron scattering experiments, have shown that an ultrasoft phonon mode exists in $CaAlSi$, but not in $SrAlSi$, which can explain the observed differences. These *ab initio* calculations so far, and analyses of the experimental data based thereon, have assumed that the stacking of Al-Si planes along the c -axis is either uniform or completely disordered.

However, recent X-ray diffraction experiments on nH- $CaAlSi$ single crystals revealed several stacking variations of the Al-Si layers, denoted as A and B in the following (see Fig. 1). The A- and B-layers differ by a 60° rotation around the c -axis. Besides the simple 1H structure characterized by a |A|A|A|... stacking, two more stacking variants were found: 5H with a AABBB and 6H with a AAABBB sequence. Stacking of the A- and B-layers induces internal stress on the structure, causing buckling of *boundary layers*, i.e., layers with an unlike neighboring layer.

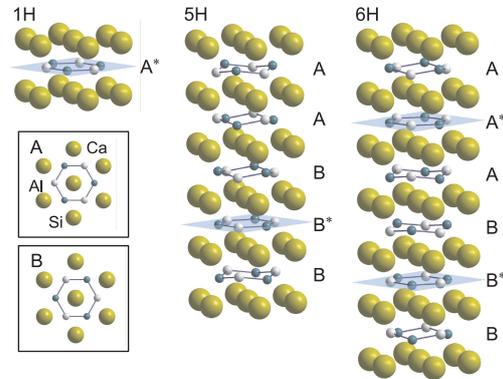


Figure 1: Crystal structure of 1H-, 5H- and 6H- $CaAlSi$, which are characterized by a different sequence of A- and B-layers. A- and B-layers are rotated by 60° around the c -axis with respect to each other. Flat and buckled Al-Si layers are indicated with and without an asterisk, respectively.

We have investigated the effects of pressure on the superconducting properties of nH- $CaAlSi$ by experiments on single crystals and *ab initio* linear-response calculations of their e-ph properties [4]. This has allowed us to understand the interplay between stacking variants, soft modes and superconductivity in nH- $CaAlSi$.

Our measurements reveal that the pressure variation of T_c in nH-CaAlSi strongly depends on the stacking sequence. Figure 2 shows the temperature dependence of the magnetic susceptibility ($\chi(T)$) of nH-CaAlSi single crystals under pressures up to ≈ 10 kbar. At ambient pressure, the T_c 's of 1H-, 5H-, and 6H-CaAlSi are 6.50 K, 5.95 K, and 7.89 K, respectively, consistent with previous reports [2]. For 1H-CaAlSi, T_c decreases linearly with a rate of $\Delta T_c/T_c = -0.03$ K/kbar. In contrast, the pressure dependence in 5H-CaAlSi is slightly nonlinear with an initial slope of $+0.013$ K/kbar, while 6H-CaAlSi exhibits a more pronounced nonlinear behavior and saturation at $T_c \approx 7.95$ K already at ≈ 10 Kbar.

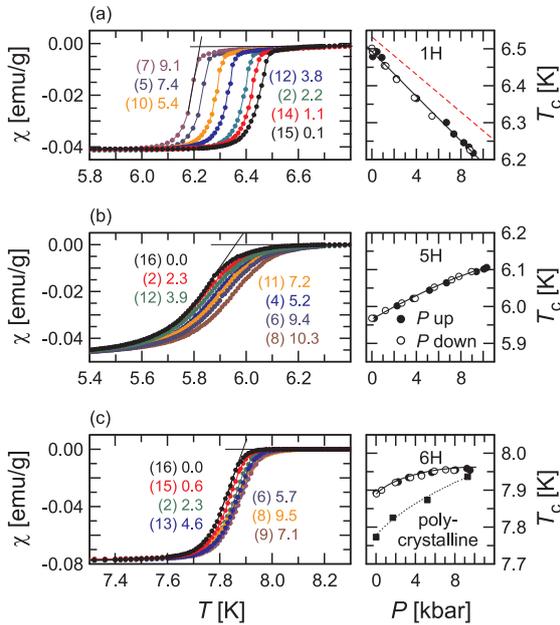


Figure 2: (color online) Left: Temperature dependence of the susceptibility for CaAlSi single crystals at different pressures. The numbers next to the data and in the parenthesis correspond to the applied pressure (kbar) and the sequential order of the measurement runs, respectively. The extrapolation method to determine T_c is demonstrated with solid lines. Right: Pressure dependence of T_c for (a) 1H-, (b) 5H-, (c) 6H-CaAlSi single crystals. For comparison we plot the previous data for polycrystalline sample from [5] in (c) and the theoretical curve for $T_c(P)$ in (a) for 1H-CaAlSi with (red) dashed line.

The decrease of T_c with P in 1H-CaAlSi is adverse both to previous reports on polycrystalline samples and to an existing *ab initio* study which predicts an abrupt increase of T_c accompanied by a lattice instability. The behavior of T_c with P in 5H- and 6H-CaAlSi suggests that also in these variants a phonon softening occurs.

Our *ab initio* calculations confirm that indeed a strong phonon softening occurs in all the identified stacking variants of CaAlSi, and that this is not sufficient to lead to an increase of T_c with P in 1H-CaAlSi. We calculated the structural, electronic and vibrational properties of nH-CaAlSi as a function of pressure, up to 100 kbar. Besides the identified 1H, 5H and 6H stacking variants, we also considered hypothetical 2H- and 3H-CaAlSi, characterized by an |AB|AB| and |AAB|AAB| stacking of the Al-Si planes, respectively. 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.

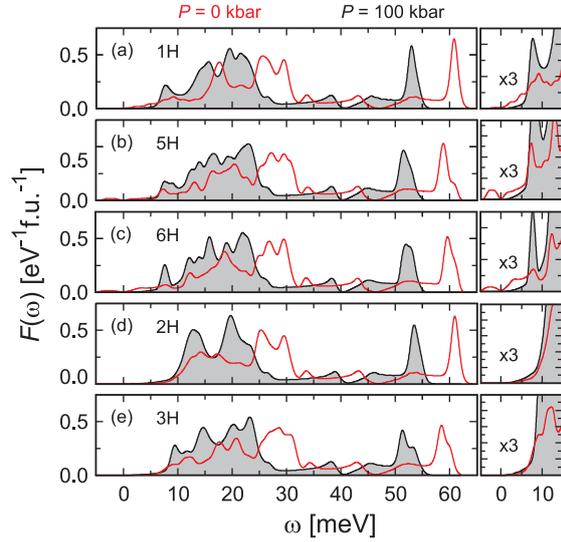


Figure 3: (color online) Linear Response Phonon DOS (phDOS) for different nH-CaAlSi at $P=0$ and $P=100$ kbar; in the right sub-panel we show an enlargement of the low-energy region.

In Fig. 3, we display the phonon density of states (DOS) 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 ≈ 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 $P \approx 80$ Kbar. The hypothetical 2H-CaAlSi and 3H-CaAlSi, on the other hand, do not display the ultrasoft phonon peak at $P=0$, and all phonon modes harden with increasing pressure.

The softening of a single phonon mode can in some cases lead to an increase of T_c with pressure. According to Hopfield's formula, the partial electron-phonon coupling associated to a single phonon mode is given by:

$$\lambda = \frac{N(\epsilon_F)D^2}{M\omega^2}, \quad (1)$$

where $N(\epsilon_F)$ is the electronic DOS at the Fermi level, D is the deformation potential, and $M\omega^2$ is twice the phonon force constant.

Usually, $N(\epsilon_F)$ decreases and ω increases with P , leading to a net decrease of λ and hence T_c . This is what happens, for example, in 2H- and 3H-CaAlSi. However, if ω of one particular phonon decreases with P , it is possible to have a net increase of T_c , if the coupling of the electrons is sufficiently strong to overcome the opposing effect of the other phonons and of the DOS.

A careful linear response calculation of the full electron-phonon spectral function $\alpha^2F(\omega)$ as a function of P shows that this does not happen in 1H-CaAlSi. In Tab. , we report the T_c of 1H-CaAlSi, estimated via the McMillan formula,

$$T_c = \frac{\langle\omega_{\ln}\rangle}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - (1+0.62\lambda)\mu^*}\right], \quad (2)$$

where ω_{\ln} is the logarithmic-averaged phonon frequency and μ^* is the Coulomb pseudopotential, fixed to $\mu^* = 0$ in the following.

Table 2:

Calculated superconducting properties of 1H-CaAlSi as a function of pressure. T_c was obtained by the McMillan formula, with $\mu^* = 0.1$. For comparison, we give in parentheses the results for 2H.

P [Kbar]	$\langle\omega_{\ln}\rangle$ [K]	λ	T_c [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)

The temperature T_c is seen to decrease with P , with $\Delta T_c/dP = -0.02$ K/kbar, in nice agreement with the experiments. This is due to a delicate balance between $\langle\omega_{\ln}\rangle$ and λ . For comparison, in the same table we also show the data for 2H-CaAlSi, which shows a much more usual behavior.

For 5H- and 6H-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, their electronic DOS's and soft mode phonon frequencies decrease with the same rate as in 1H-CaAlSi. For this reason, we assume that their $\alpha^2F(\omega)$'s have very similar characteristics to that of 1H-CaAlSi. A simple model, based on a Gaussian decomposition of the $\alpha^2F(\omega)$ of 1H-CaAlSi, shows that the different pressure dependence of T_c for 5H and 6H can be explained assuming an increasing behavior of the spectral weight for the ultrasoft phonon mode under pressure. This could reflect either small differences in the electron-phonon matrix elements due to the buckling of some planes, or a different number of phonon modes that soften under pressure.

Our calculations thus show the identified stacking variants of nH-CaAlSi have very similar electronic and vibrational properties; the differences in their superconducting properties reflect small details of the e-ph interaction. In contrast, 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.

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