

Pressure Effects on the Superconducting transition in nH -CaAlSi

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 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 , 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]

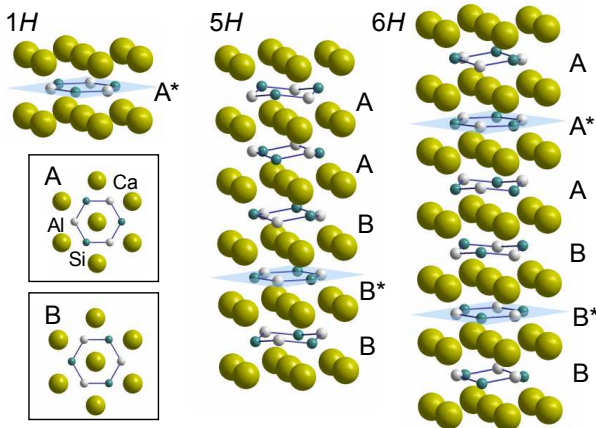


Figure 1: Crystal structure of $1H$, $5H$ and $6H$ - CaAlSi, which are characterized by a different sequence of A- and B-layers. A- and B-layers are rotated by 60° around the c -axis with respect to each other. Flat and buckled Al-Si layers are indicated with and without an asterisk, respectively.

CaAlSi has recently attracted considerable interest, because it exhibits an ultrasoft phonon mode and crystallizes with several stacking variants. Thermodynamic experiments on polycrystals 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 ultra-soft phonon mode, with $\omega \sim 7$ meV exists in CaAlSi, but not in SrAlSi, which can explain the observed differences. These *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.

However, recent X-ray diffraction experiments on nH -CaAlSi single crystals revealed several stacking

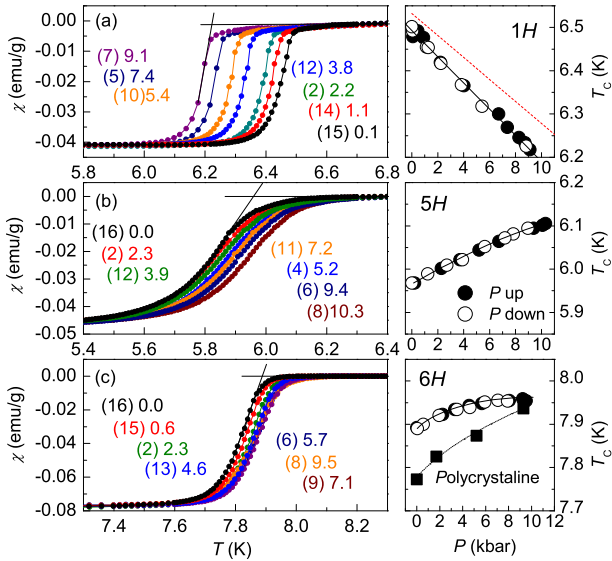


Figure 2: (color online) *Left*: Temperature dependence of the susceptibility for CaAlSi single crystals at different pressures. The numbers next to the data and in the parenthesis correspond to the applied pressure (kbar) and the sequential order of the measurement runs, respectively. The extrapolation 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 (Ref. [?]) in (c) and the theoretical curve for $T_c(P)$ in (a) for 1H-CaAlSi with (red) dashed line.

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 an internal stress on the structure, causing a buckling of *boundary layers*, i.e. layers with an unlike neighboring layer.

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 of nH -CaAlSi strongly depends on the stacking sequence. Figure 2 shows the temperature dependence of the magnetic susceptibility ($\chi(T)$) of single crystals of nH -CaAlSi 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; 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 ~ 10 Kbar.

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 behaviour 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-

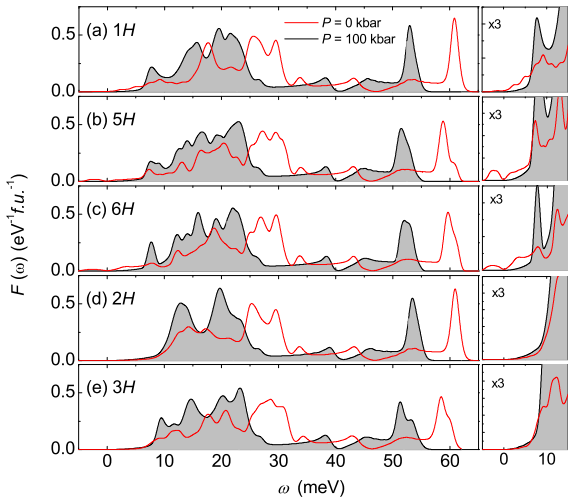


Figure 3: (color online) Linear Response Phonon DOS (phDOS) for different nH -CaAlSi at $P=0$ and $P=100$ kbar; in the right sub-panel we show an enlargement of the low-energy region.

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.

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 ~ 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. 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.

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

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

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

Usually, $N(\varepsilon_F)$ 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 the 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 table 1, we report the T_c of $1H$ -CaAlSi, estimated via the Allen-Dynes formula,

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

where ω_{ln} is the logarithmic-averaged phonon frequency and μ^* is the Coulomb pseudopotential, fixed to $\mu^* = 0.1$ in the following.

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)

Table 1: Calculated superconducting properties of $1H$ -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 $2H$.

T_c is seen to decrease with P , with $\Delta T_c/dP = -0.02$ K/kbar, in nice agreement with experiment. 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 behaviour.

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 $\alpha^2 F(\omega)$'s have very similar characteristics to that of $1H$ -CaAlSi. A simple model, based on a Gaussian decomposition of the $\alpha^2 F(\omega)$ 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 ultra-soft phonon mode under pressure. This 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.

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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