Electrons, Phonons and Stability of CaAl$_{2-x}$Si$_x$.

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Abstract

Il seguente lavoro[1] riporta un dettagliato studio da principi primi delle proprietà strutturali, elettroniche e vibrazionali della lega superconduttiva ternaria CaAl$_{2-x}$Si$_x$, considerata nella fase C$_{32}$. Tale analisi considera sia l’intervallo di drogaggio 0.6 $\leq$ x $\leq$ 1.2 per il quale la lega è stata sintetizzata, sia il limite teorico di elevata concentrazione di alluminio o silicio. Nell’intervallo sperimentale di drogaggio, la dipendenza delle proprietà elettroniche dalla diversa composizione è accuratamente descritta mediante un modello a bande rigide che perde invece di validità sia per x $\leq$ 0.6 che per x $\geq$ 1.2. Nel caso di elevate concentrazioni di alluminio, tale fallimento risulta essere correlato alla comparsa di instabilità vibrazionali e determina importanti differenze tra il CaAl$_2$ e l’ MgB$_2$.

We report[1] a detailed first-principles study of the structural, electronic and vibrational properties of the superconducting C$_{32}$ phase of the ternary alloy CaAl$_{2-x}$Si$_x$, both in the experimental range 0.6 $\leq$ x $\leq$ 1.2, for which the alloy has been synthesized, and in the theoretical limits of high aluminium and high silicon concentration. In the experimental range, the dependence of the electronic bands on composition is well described by a rigid-band model, which breaks down outside this range. Such a breakdown, in the (theoretical) limit of high aluminium concentration, is connected to the appearance of vibrational instabilities, and results in important differences between CaAl$_2$ and MgB$_2$.

The discovery [2] of superconductivity with a $T_c$ of 39 K in MgB$_2$ in 2001 came somehow unexpected: a simple s – p binary compound, without d electrons, showed a critical temperature which was higher than the all the known electron-phonon superconductors and comparable to those of the first high-$T_c$ cuprates.

The crystal structure of magnesium diboride, known as C$_{32}$ [3] (Fig. 1), with hexagonal boron planes intercalated with magnesium atoms, is analogous to that of graphite, and common to many binary and ternary compounds, some of which contain light s – p elements.

One of these compounds, the CaAlSi alloy, has been recently synthesized [4] in the C$_{32}$ structure in a wide composition range (x), and shown to be superconducting at all x, with $T_c$ reaching a maximum [4] of 7.7 K at x = 1.
First-principles calculations [6] [5] at \(x = 1\) have shown that also in this case superconductivity is of electron-phonon type, and that the lower critical temperature with respect to MgB\(_2\) can be understood because the electronic and vibrational states involved in the superconducting pairing are different.

However, since these calculations were carried out only at a single composition, there has been so far no attempt to characterize the complete phase diagram of this alloy: in this work, we performed an extensive ab-initio analysis of CaAlSi, both inside and outside the experimental range of stability, in the limits of high Si \((x=2)\) and Al \((x=0)\) concentrations. The latter is of particular interest, because, in this structure, CaAl\(_2\) would be isostructural and isostructural to MgB\(_2\), and thus represent an ideal candidate for the observation of superconductivity.

The calculations reported in this work were carried out in the framework of density functional perturbation theory [7] using two different plane-waves codes, ABINIT [8] and PWSCF [9], and pseudopotentials generated with the FHI98 code [10]. For the description of doping, we used the Virtual Crystal Approximation [11], as implemented in the ABINIT code. Further details can be found in Ref. [1]. Calculations were performed on the CINECA-CLX (IBM Linux Cluster 1350); an average single run for a linear-response calculation required 36 hours/node.

In order to investigate the relation between the stability of the C\(_{32}\) structure and composition, we considered a dense grid of \(x\) values between 0 and 2, and for each of these values we optimized the internal parameters of the crystal structure. In the optimized structure we calculated the band structure and
phonon spectrum, to test for the occurrence of dynamical lattice instabilities. Our results, summarized in Fig 2-5, show that the stability of this compound is governed by an interlayer band, which is empty in MgB$_2$, coupled to an out-of-plane buckling phonon, which becomes unstable at low $x$. The same phonon is also mainly responsible for superconductivity. The coupling of out-of-plane phonons to interlayer states and their consequent instability is likely to be a general property of the C$_{32}$ phase. The main result of this work is thus that the interlayer band, empty in MgB$_2$, and the “out-of-plane” phonons (optical $B_{1g}$ and acoustical $A_{2u}$ at $\Gamma$), irrelevant for superconductivity in MgB$_2$, play a major role on the stability and superconductivity of C$_{32}$ intermetallic compounds, once the structural parameters $c$ and $a$ assume appropriate values. This observation goes beyond the CaAlSi family and represents the starting point for further studies of a wider class of hexagonal, graphite-like compounds. [14]

Figure 2: Comparison between the Density of States (DOS) at the Fermi level of CaAlSi obtained by a fully self-consistent calculation and a rigid band model (see text). Our results show that the rigid-band model breaks down precisely at the border of the experimental range of stability of this compound.

References


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Figure 3: Band structure of CaAlSi at $x=1$: the $sp^2$-hybrids of Al and Si form three bonding $\sigma$ bands while the $2p_z$ states of Al and Si form a bonding ($\pi$) and an antibonding ($\pi^*$) band. A second band crosses the Fermi level, its bottom has a prevailing Ca $3d_{\frac{z^2-r^2}{2}}$ character, yet the band as a whole may be easily traced back to the so-called graphite interlayer band [12]; the rigid-band model based on this picture breaks down precisely outside the experimental range of stability of the alloy in this structure.


[8] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors. URL http://www.abinit.org/.

Figure 4: Optimized lattice parameters of CaAl$_{2-x}$Si$_x$ in the C$_{32}$ structure as a function of composition $x$: the $a$ lattice parameter monotonically increases as $x$ decreases, while $c$ strongly decreases below $x = 0.5$ until it equals $a$ at $x \approx 0.3$ and then abruptly falls: around $x < 0.15$ there is a sudden jump in the $c/a$ ratio, from $\sim 1$ to $\sim 0.8$. As discussed, for example, by Pearson [13], compounds which crystallise in the C$_{32}$ structure are divided in two branches: the AlB$_2$ branch, with $c/a > 0.95$ and the UHg$_2$ branch, $c/a < 0.90$, separated by a forbidden range of $c/a$ values.


Figure 5: Selected phonon frequencies of CaAl$_{2-x}$Si$_x$ as a function of composition. The compound is dynamically stable (all frequencies are real) down to $x = 0.15$, where the mode involving out-of-plane vibrations of the Al/Si atoms becomes unstable in the upper half of the Brillouin zone (imaginary frequencies, here shown as negative). Note that the transition seems to be first-order, like that in the $c/a$ ratio. Notice also that at $x = 0$ (CaAl$_2$) the compound is dynamically unstable.