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

Matteo Giantomassi

INFM Center for Statistical Mechanics and Complexity and Dipartimento di Fisica, Università di Roma "La Sapienza", Piazzale A. Moro 2, I-00185 Roma, Italia
Istituto dei Sistemi Complessi, CNR, Via dei Taurini 19, 00185 Roma, Italia
Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

Lilia Boeri

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stoccarda, Germania

Giovanni B. Bachelet

INFM Center for Statistical Mechanics and Complexity and Dipartimento di Fisica, Università di Roma "La Sapienza", Piazzale A. Moro 2, I-00185 Roma, Italy

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 instabillità 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 synthesised, 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 isoelectronic 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.
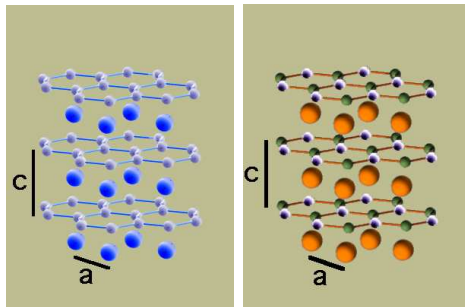

Figure 1: Left: crystal Structure of MgB_2 (C_32 phase): Hexagonal planes of B atoms (violet) are intercalated by Mg (blue) atoms. Right: For $x = 1$ the $CaAl2-xSix$ alloy prefers an ordered phase of lower symmetry, with alternated Al and Si (white, green) occupying the B sites in the hexagonal plane and Ca (orange) replacing Mg, but for $x \neq 1$ the Boron sites are randomly occupied by Al or Si atoms and on average (VCA) the struture is C_32 (left). At x=0, with 8 valence electrons, $CaAl_2$ is isoelectronic with MgB_2. The (c/a) ratio is 1.142 in MgB2, while it varies strongly in CaAlSi (see fig. 4).

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 Γ), 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]
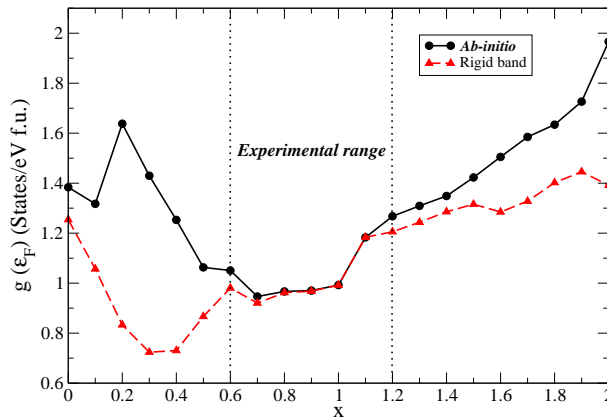

Figure 2: Comparison between the Density of States (DOS) at the Fermi level of CaAlSi obtained by a fully self-consistent calculation and a rigid band model (see text). Our results show that the rigid-band model breaks down precisely at the border of the experimental range of stability of this compound.

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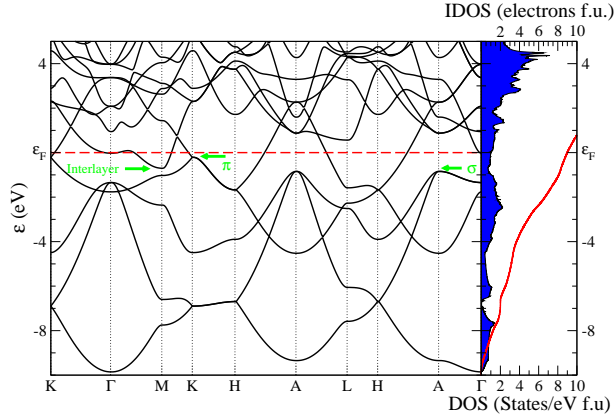[2] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu. *Nature (London)*, **410**:63, (2001)

Figure 3: Band structure of CaAlSi at $x=1$: the sp^2-hybrids of Al and Si form three bonding σ bands while the $2p_z$ states of Al and Si form a bonding (π) and an antibonding ($\pi^\star$) band. A second band crosses the Fermi level, its bottom has a prevailing Ca $3d_{z^2-r^2}$ 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.

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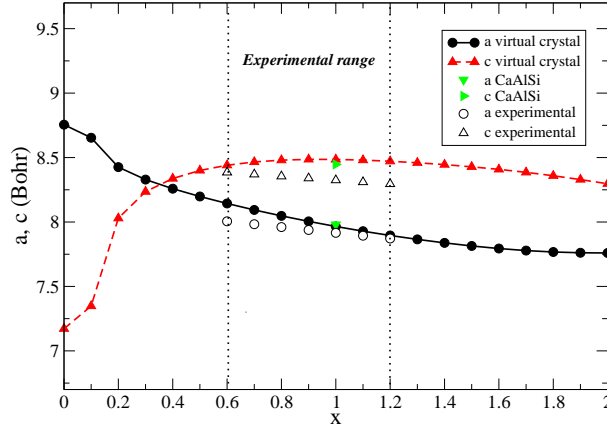
Figure 4: Optimized lattice parameters of $CaAl_{2-x}Si_x$ in the C_{32} structure as a function of composition x: the a lattice parameter monotonically increases as x decreases, while c strongly decreases below $x = 0.5$ until it equals a at $x \sim 0.3$ and then abrupty falls: around $x < 0.15$ there is a sudden jump in the c/a ratio, from ~ 1 to ~ 0.8. As discussed, for example, by Pearson [13], compounds which crystallises 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.

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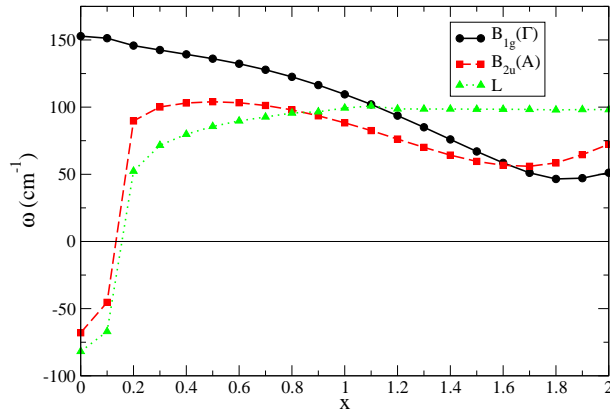[14] L. Boeri, M. Giantomassi, G.B. Bachelet, and O.K. Andersen. *Unpublished.*

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.