The recent discovery of superconductivity in Ca- and Yb-intercalated graphite has refocused considerable interest onto graphite intercalated compounds (GICs). The superconducting transition temperatures $T_c$ in Ca and Yb GICs, CaC$_6$ and YbC$_6$, amount to $\approx 11.5$ and $6.5$ K, respectively (Fig. 1), significantly higher than those of the alkali-metal intercalated graphite phases studied in the 1980’s. Similar to the 40 K superconductor MgB$_2$ where the hexagonal B sheets are intercalated with Mg, the alkaline-earths atoms in CaC$_6$ and YbC$_6$ are sandwiched by the honeycomb graphene layers (Fig. 1). The intercalated metal ions act as donors and transfer charge into the host graphene layers, resulting in partially filled graphene bands.

Apart from the significant enhancement of $T_c$ as compared to alkali-metal systems of the 1980’s, two other aspects immediately attracted attention: In case of YbC$_6$ it was initially speculated that 4$f$-electrons may play a role and that superconductivity might be mediated by valence fluctuation. This possibility, however, could be ruled out and it was found that Yb, like Ca, is divalent and the $f$-electrons provide no essential contributions to the electronic structure at $E_F$.

The second interesting aspect concerned the role of the so-called ‘inter-layer band’, i.e. a three-dimensional nearly-free electron band emerging from electrons localized in the intercalant plane, and its relation to superconductivity together with the conjecture of an unconventional electronic pairing mechanism involving excitons. This conjecture was questioned based on the results of the first heat capacity study on CaC$_6$ carried out in Stuttgart [1]. It clearly resolved the anomaly at $T_c$ and proved the bulk nature of the superconductivity (Fig. 2).
Figure 3: (a) Temperature dependence of the susceptibility for CaC$_6$ (sample S1) at different pressures. The numbers next to the data and in the bracket corresponds to the applied pressure (kbar) and the sequential order of the measurement runs. $T_c$ is determined as the temperature where the extrapolation of the steepest slope of $\chi/B_4T/B_5$ intersects the extrapolation of the normal state $\chi/B_4T/B_5$ to lower temperatures. (b) Pressure dependence of $T_c$ for three CaC$_6$ samples. The filled and open symbols are data taken at increasing and decreasing pressure, respectively. The dashed lines are guides to the eyes. The inset shows the relative change of $T_c$ with pressure. In addition, the analysis of the temperature and the magnetic field dependence of heat capacity of CaC$_6$ strongly evidence a fully gapped, intermediate-coupled, phonon-mediated superconductor without essential contributions from alternative pairing mechanisms. The degree of filling of the inter-layer bands, crucial for the conjectured acoustic plasmon pairing mechanism, depends not only on the charge transfer from the intercalant, but also on the separation of the graphene sheets. By applying hydrostatic pressure the graphite layer spacing, and hence the energy of the inter-layer bands, can be continuously tuned without affecting the chemical composition. On the other hand, a comparison of the pressure dependence of $T_c$ with the results of first-principles calculations of the electronic and vibrational properties of the GICs could support or rule out the hypothesis of an e-ph mediated coupling mechanism.

The effect of pressure on $T_c$ of CaC$_6$ has been investigated up to $\approx 16$ kbar. $T_c$ is found to increase under pressure with a large relative ratio $\Delta T_c/T_c$ of $\approx +0.4$ (Fig. 3). First-principles calculations carried out in the department Andersen show that the positive effect of pressure on $T_c$ can be explained within the scope of electron-phonon theory due to the presence of a soft phonon branch associated to in-plane vibrations of the Ca atoms [2].

Figure 4: (a) Temperature dependence of the ac susceptibility of SrC$_6$ for various magnetic fields (as indicated) perpendicular to the c-axis. (b) $H_{c2}$ for $H \perp ab$-plane and $H \perp c$-axis. The Werthamer-Helfand-Hohenberg predictions for both field directions are shown as (red) solid lines. (c) Temperature dependence of $\Delta C_p/T = C_p(H=0)/T - C_p(500 \text{ Oe})/T$. The (blue) dashed and (red) solid lines are the BCS curve and the best fit according to the $\alpha$-model, respectively. The inset shows the temperature dependence of $C_p$ at $H = 0$ and 500 Oe. The solid (black) line through the data points for $H = 500$ Oe is a fit to a polynomial.
Another way to modify the relevant phonon modes is to vary the intercalant species and replace Ca with other alkaline-earths such as Sr or Ba. Mazin pointed out that for CaC\textsubscript{6} and YbC\textsubscript{6} the square root of the mass ratio of the intercalants is only 15\% larger than the ratio of their \(T_c\)’s. Thus, according to this ‘isotope’ effect argument other alkaline-earths GICs may as well be superconducting. In fact, subsequent\textit{ab-initio} calculations by Calandra et al. suggested superconductivity for SrC\textsubscript{6} and BaC\textsubscript{6}.

Lately, we prepared high-quality samples of SrC\textsubscript{6} and BaC\textsubscript{6} and found superconductivity in SrC\textsubscript{6} at \(T_c = 1.65(6)\) K by susceptibility and specific heat measurements but no indication of superconductivity in BaC\textsubscript{6} down to \(\approx 0.3\) K (Fig. 4). The superconducting properties of SrC\textsubscript{6} as well as the results of our\textit{ab-initio} calculations clearly demonstrate that SrC\textsubscript{6} can serve as a reference system to better understand the \textit{unconventional} nature of superconductivity in CaC\textsubscript{6} [3].

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