Electronic structure of the superconducting graphite intercalates

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Outline

1. Background
2. Electronic structure of GICs
3. Mechanism of pairing: Room for Novelty?
4. Perspectives and Summary
1841: GICs first synthesized\(^a\)
1965: alkali-intercalated graphite compounds found to superconduct\(^b\) with a low \(T_c \sim 0.1\text{K}\): e.g. \(\text{C}_8\text{K}, \text{C}_6\text{Cs}, \text{C}_6\text{Rb}, \ldots\)\(^c\)
1989: Highest \(T_c = 5\text{K}\) achieved in \(\text{C}_2\text{Na}\) under pressure\(^d\)

\(^a\)Schafhütl, 1841
\(^b\)Hannay et al., 1965
\(^c\)for review see Dresselhaus & Dresselhaus, 2002
\(^d\)Belash et al., 1989
Recently, two compounds discovered (C$_6$Yb & C$_6$Ca) with $T_c$ (6.5K & 11.5K) two orders of magnitude higher than, e.g., C$_8$K$^a$

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**Questions**

1. Does superconductivity in GICs share a common origin?
2. If so, why is range of $T_c$ so wide?
3. Why are some GICs non-superconducing?
4. What clues are provided by electronic structure?
Comparison of *empty* graphite & Ca identifies states at Fermi level

Charge transfer from Ca shifts Fermi level into graphite $\pi^*$ band; in addition, dispersive Ca $3d$-like *interlayer* bands become occupied.
Comparison of empty graphite & Ca identifies states at Fermi level

Similar phenomenology applies to C₆Yb

Electronic structure of C₆Ca
Evidence for the role of the interlayer state
Model of interlayer band occupancy
Amongst class of superconducting GICs, what makes $C_6Ca$ and $C_6Yb$ so special viz. $T_c$?

And why aren’t all GICs found to be superconducting?

To address these questions, it is instructive to compare electronic structures of the family of Li-based GICs.
Although $C_6\text{Li}$, $C_6\text{Li}_2$ and $C_6\text{Li}_3$ can be prepared, only $C_6\text{Li}_3$ superconducts ($T_c \approx 1.9\text{K}$).

- Again, electrons transferred to graphite $\pi^*$ band
- Electron transfer plus enhanced c-axis spacing lowers a Li $2s$-like interlayer band
- This band is only occupied in $C_6\text{Li}_3$
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Electronic structure of the superconducting GICs
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Evidence for the role of the interlayer state.
Could the occupation of the interlayer band be significant?
In all those, and only those, compounds that superconduct, the interlayer state is found to be occupied.
Intuition from graphite

- In addition to the tight-binding $\sigma$ and $\pi$ bands, graphene has an unoccupied surface-like band\textsuperscript{a}
- In pure graphite, these states form a nearly free-electron like interlayer band seen experimentally in photoemission\textsuperscript{b}

\textsuperscript{a}Posternak \textit{et al.} 1983, Holzwarth \textit{et al.} 1984
\textsuperscript{b}see, e.g., Reich \textit{et al.} 1986
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Phase diagram of empty graphite

Electron doped, transfer of carriers into $\pi^*$ band combined with increased c-axis spacing results in lowering of the interlayer band.

Data from GICs shows model captures much of the phenomenology.
Room for novelty?

- Available mechanisms constrained by:
  - apparent necessity to occupy states in interlayer region
  - observed range of $T_c$ — spans more than two decades while material properties (viz. DoS, etc.) change little

- Previous studies\textsuperscript{a} have shown that aspects of superconductivity in GICs can be accommodated by two-band phenomenology

- But what about microscopic theory?

\textsuperscript{a}Al Jishi, 1983; Al Jishi & Dresselhaus, 1982
Phonons?

- Recent *ab-initio* study of $C_6Ca^a$ implicate phonon mediated mechanism: Ca (in-plane) & C (out-of-plane)

\[{}^a\text{Calandra & Mauri, '05}\]

- quantitative(!) prediction for $T_c$...
- Yet, by itself, this does not explain observed range of $T_c$ & necessity to populate interlayer band
- Moreover, parallel calculations for other GICs remain open
Remote from graphene layer, one might expect “native” interlayer states to couple weakly to lattice...

However, weak coupling provides ideal environment for soft charge fluctuations which could promote superconductivity via excitonic pairing mechanism\(^a\)

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\(^a\)Allender, Bray & Bardeen, ’73, Takada, ’77, Kresin & Morawitz, ’88, ...
Carbon nanotubes

- “Interlayer states” find counterpart in carbon nanotubes as nearly free-electron states within and outside tube\(^a\)

\(^a\) Miyamoto et al., '95
Intercalation?

Phenomenology of doped empty nanotube similar to GICs

$^a$Csányi et al. unpublished
Superconductivity?

- Superconductivity has been reported in 4Å tubes in the zeolite AFI\textsuperscript{a}
- Preliminary calculations suggest it is not related to the interlayer state\textsuperscript{b}
- Several experimental groups pursuing the doping approach

\textsuperscript{a}Tang et al.
\textsuperscript{b}Pickard et al., unpublished
The interlayer state

- It is tempting to look for a common phenomenology in MgB$_2$
- MgB$_2$ indeed possesses interlayer states
- But they remain unoccupied
- Instead, charge transfers from $\sigma$ to $\pi^*$, and the $\sigma$ holes couple strongly to the lattice
Summary

- Electronic structure calculations provide compelling evidence for importance of interlayer band for superconductivity.
- On this basis, numerical work already being used to guide experimental search for new GIC superconductors.
- Preliminary electronic structure calculations suggest a phonon-mediated mechanism...
- ...which relies on coupling of interlayer band to metal ion phonons.
- Phenomenology of GICs points the way towards possible superconductivity in carbon nanotube intercalate compounds.