“Standard Model” for Superconductivity in Graphite Intercalation Compounds: Prediction of Optimum $T_c$

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ISSP Main Building 6F Rm. A615
16:00-17:00, 23 January 2009

Outline
1. Introduction
   $T_c = 0.15K$ or less for alkali intercalated graphite (KC$_8$ etc.)
   $T_c > 10K$ (enhanced by 100 times) for CaC$_6$ found in 2005

2. Explanation of the “Standard Model”
   Proposed in 1982 to account for KC$_8$ and RbC$_8$: YT, JPSJ 51, 63.

3. Calculated Results for $T_c$ for Existing Graphite Intercalation Compounds (GICs)
   $T_c$ can be reproduced also for CaC$_6$ with my old model.

4. Identification of Key Controlling Parameters to Enhance $T_c$ in CaC$_6$, Compared to KC$_8$
   “What is the maximum $T_c$ in this class of materials?”
   Perspectives for higher $T_c$ reaching near 100K cf. YT, JPSJ 78, 013703 (2009).

5. Summary and Discussion

Alkali Intercalated Graphite: Before 1980

KC$_8$ (1st stage): found to superconduct in 1965 with $T_c = 0.15K$.
RbC$_8$, CsC$_8$: superconduct, but $T_c$ is much less than 0.1K.
LiC$_6$, KC$_{16}$ (2nd stage), KC$_{24}$ (3rd stage) etc.: do not superconduct.

$T_c$ depends rather strongly on samples:
KC$_8$: 0.08 - 0.55K  ($\rightarrow 0.15K$)
RbC$_8$: 0.023 - 0.151K  ($\rightarrow 0.026K$)
CsC$_8$: 0.02 - 0.135K

MC$_8$

[$M = K, Rb, Cs$

$d = 5.42-5.94\text{Å}$

Alkali Intercalated Graphite: 80s-90s

LiC$_2$: found to superconduct in 1989 with $T_c = 1.9K$.
Some other superconductors with $T_c$ around 1K are also found in this class of materials in 80s and 90s.

$LiC_2$ $d = 3.7\text{Å}$

[$T_c$ vs. $d$]

[$KC_8$, $RbC_8$, $CsC_8$, $LiC_2$]
Alkaline-Earth Intercalated Graphite

**Breakthrough in 2005:**
- **CaC$_6$:** $T_c = 11.5$K \[\text{[Weller et al., Nature Phys. 1, 39(2005); Emery et al., PRL 95, 087003(2005)]}\]
- **YbC$_6$:** $T_c = 6.5$K \[\text{[Gauzzi et al., PRL 98, 067002(2007)]}\]
- **SrC$_6$:** $T_c = 1.65$K \[\text{[Kim et al., PRL 99, 027001(2007)]}\]

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**Electronic Band Structure: LiC$_2$ and LiC$_6$**

**Band calculation:**
- LiC$_6$, LiC$_2$: [Csanyi et al., Nature Phys. 1, 42 (2005)]

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**Electronic Band Structure: KC$_8$**

**Band calculation:**
- KC$_8$: [Ohno et al., JPSJ 47, 1125(1979); Wang et al., PRB 44, 8294(1991)]

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**Electronic Band Structure: CaC$_6$, YbC$_6$**

**Important common features**
1. 2D- and 3D-electron systems coexist.
2. Only 3D electrons in the interlayer band superconduct.

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**Superconductivity in GICs (Takada)**

- Coexistence of 2D and 3D electrons
- The interlayer band is much modified due to the mixing with the d bands of Ca atom. \( m \sim 3m_e \)
Comparison with MgB₂

In MgB₂, the 2D σ bands (which are known to be the main superconducting bands) come at the Fermi level due to the difference in the total electron number.

Superconductivity in GICs (Takada)

Phonon Mechanism

Phonon mechanism of superconductivity for CaC₆ is proposed by calculating the Eliashberg function $\alpha^2 F(\omega)$:

- Mazin, PRL 95, 227001 (2005);
- Calandra & Mauri, PRL 95, 237002 (2005);
- Sanna et al., PRB 75, 020511(R) (2007).

Confirmed by the observation of the isotope effect ($\alpha \approx -0.5$) on Ca, (but a very small isotope effect on C, indicating a minor role of C-related modes):

- Hinks et al., PRB 75, 014509 (2007).

Main features:
1) Low-energy Ca modes
2) Low-energy interlayer C modes
3) High-energy intralayer C modes

But this $\lambda$-$\mu$ game does not provide us really important aspects of the problem. (Generally the screening effect on $\lambda$ is not properly treated.)

"Why is $T_c$ so much enhanced?"

→ Needs much more work!

Superconductivity in GICs (Takada)

Aims of This Talk

Issues to be discussed:

1) A simple “standard model” (focusing on the intercalant modes and the low-energy interlayer C modes) is introduced for providing a unified view of superconductivity in GICs with $T_c$ ranging three orders of magnitude.

2) Key parameters to enhance $T_c$ by two orders from KC₈ to CaC₆ will be clarified in this standard model.

3) Some discussions are given to maximize $T_c$ with a prediction of its maximum value in GICs.

Model for GICs: MCₓ

This model was proposed already in 1982 for explaining superconductivity in MC₈ ($M=K,Rb,Cs$): YT, JPSJ 51, 63 (1982)

Superconductivity in GICs (Takada)
Hamiltonian for the Model

\[ H = \sum_{p'p} t_{p'p} c_{p'}^\dagger c_{p} + \sum_{p'p} t_{p'p} c_{p'}^\dagger c_{p} + \sum_{p'p} \sum_{\omega} \omega_{p'} b_{p'}^\dagger b_{p} + H_{\text{el-\text{el}}} + H_{\text{el-ph}} \]

\[ H_{\text{el-\text{el}}} = \frac{1}{2} \sum_{p'p} \sum_{\omega} \sum_{\omega'} \sum_{\omega''} V(q, q') c_{p'}^\dagger c_{q'} c_{p} c_{q'} c_{p'}^\dagger c_{q'} c_{p'} \]

\[ H_{\text{el-ph}} = \sum_{p'p} \sum_{\omega} \sum_{\omega'} \sum_{\omega''} V(q, q') c_{p'}^\dagger c_{q'} c_{p} c_{q'} c_{p'}^\dagger c_{q'} c_{p'} \]

Effective Interaction

The electron-electron effective interaction is calculated in the RPA with taking the layer structure into account, amounting to the \(G_0 W_0\) (one-shot GW) approximation.

\[ V(Q, i\Omega) = \frac{V^0(k, q)}{e (k, i\Omega)} \left\{ 1 - \Pi_{2D}(k, i\Omega) U_J(k, i\Omega) \left[ 1 + \Pi_{2D}(k, i\Omega) \sum_{p} U_J(k, i\Omega) \right] \right\} \]

\[ V^0(k, q) = 4\pi e^2 \left( E_n^2 q^2 + E_l^2 q^2 \right), \quad E_n(k,\omega) = 1 + \sum_{\omega' \in \epsilon} \frac{G_{2D}(k)^2}{\omega - \omega_\epsilon(k,\omega')} \]

Gap Equation

First-principles calculation of \( T_c \) is done without employing the concept of the Coulomb pseudopotential \( \mu^* \).

Anomalous Green's Function:

\[ F(k, \omega) = -G(k, \omega) G(-k, -\omega) T \sum_{p', p''} \frac{1}{\epsilon_{p'}} F(k, p', \omega) F(p'', -\omega) \]

\[ \Delta(p) = 2|\epsilon_p| \int_0^{T_c} \frac{dt}{\pi} \text{Im} F(p, \omega) \]

At \( T=T_c \):

\[ \Delta(p) - \sum_{p'} \frac{\Delta(p')}{2\epsilon_{p'}} \to \frac{\Delta(p)}{2\epsilon_{p'}} \]

Pairing Interaction:

\[ V_{p,p'} = V^0(p-p') \int_0^{T_c} \frac{dt}{\pi} \text{Im} F(p, \omega) F(p', -\omega) \]

The resulting gap equation is very similar to the one proposed in the density functional theory for superconductivity by Gross.

Polar-Coupled Phonon Mechanism

Derivation of this gap equation is given in: YT, JPSJ 45, 786 (1978)

\( \rightarrow \) Possibility of a negative \( \mu^* \) in the low-density electron gas ("Plasmon mechanism" of superconductivity)

Its successful application to polar semiconductors such as \( \text{SrTiO}_3 \) is explained in: YT, JPSJ 49, 1267 (1980).

\[ n \sim 10^{20} \text{cm}^{-3}, \quad \text{SrTiO}_3 \]

\[ n \sim 2 \times 10^{22} \text{cm}^{-3}, \quad \text{CaC}_6 \]

Stress-induced ferroelectric transition

\( \rightarrow \) softening the polar optic mode

\( \rightarrow \) bringing about superconductivity

\[ \text{In SrTiO}_3, \quad n \sim 10^{20} \text{cm}^{-3}, \]
Although the one-electron dispersion is isotropic, the effective interaction is anisotropic, leading to an anisotropic gap equation.

### Parameters to be Specified in this Model for $MC_x$

For the intercalant element $M$,
1. Valence $Z$, determining the coupling strength as well as the electron density
2. Atomic mass $m_M$, determining the phonon energies as well as the coupling strength
3. Layer separation $d$ (as well as $x$), determined by the ion size
4. Fraction separation $f$, determined by the band calculation
5. Effective mass of the 3D electron $m^*$, determined by the band calculation (using the DOS at the Fermi level or the $E_F$ itself)

<table>
<thead>
<tr>
<th>$K$ (Alkali GICs)</th>
<th>Ca (Alkaline-earth GICs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$</td>
<td>1</td>
</tr>
<tr>
<td>$d$</td>
<td>$\sim 5.5\text{A}$</td>
</tr>
<tr>
<td>$f$</td>
<td>$\sim 0.6$</td>
</tr>
<tr>
<td>$m^*$</td>
<td>$\sim m_e$ (s-like electron)</td>
</tr>
</tbody>
</table>

$K$ (Alkali GICs)

- For $K_{C_8}$, $Rb_{C_8}$, $Cs_{C_8}$, the results are just the same as those in 1982.
- For $Li_{C_2}$, our result is of the same order of the experimental result.

**Superconductivity in GICs (Takada) 17**

**Superconductivity in GICs (Takada) 18**

**Superconductivity in GICs (Takada) 19**

**Superconductivity in GICs (Takada) 20**

This model reproduces $T_c$ for both alkali and alkaline-earth GICs!!

- Smaller $f$ is favorable, because the screening effect of 2D electrons is weaker.
- Doubling $Z$ enhances $T_c$ by a factor of ten.
- Tripling $m^*$ enhances $T_c$ by another factor of ten.
- “Isotope effect”: Ca ($A=40.1$) vs Yb ($A=173.0$) $\Rightarrow \alpha \sim 0.5$
Perspectives for Higher $T_c$

For stronger interaction, lighter atoms with larger valence are favorable, but the most important parameter is $m^*$. Because $m^*$ will not become heavy without the contribution of d- or f-like electrons, light atoms may not be very promising for very high $T_c$.

Summary and Discussion

1. A successful model is explained for superconductivity in GICs with $T_c$ ranging over three orders of magnitude.
2. A very important effect of the effective mass $m^*$ of the 3D electrons on $T_c$ is revealed.
3. Some prospects of higher $T_c$ are discussed.

(1) Ti or V in graphite?
(2) Three-element GICs composed of light and heavy atoms?
(3) Improvement on the computer power by a million times in the past 30 years enables me to calculate these results very efficiently. I hope that more complex actual crystal structures can be treated in the same framework.