## ISSP Theory Seminar

# "Standard Model" for Superconductivity in Graphite Intercalation Compounds: Prediction of Optimum $T_c$


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*ISSP Main Building 6F Rm. A615*
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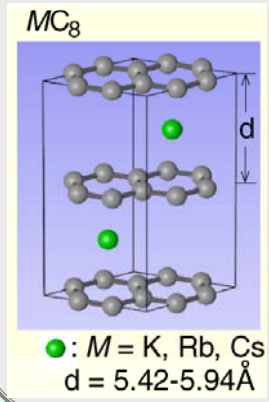
## Outline

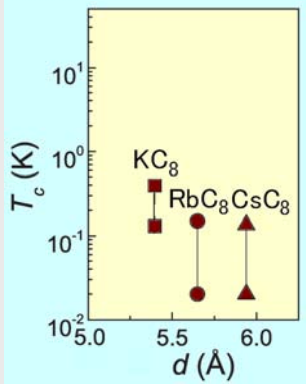
1. **Introduction**
   - $T_c$ = 0.15K or less for alkali intercalated graphite ($KC_8$ *etc.*)
   - $T_c$ > 10K (enhanced by 100 times) for $CaC_6$ found in 2005
2. **Explanation of the "Standard Model"**
   - Proposed in 1982 to account for $KC_8$ and $RbC_8$: YT, *JPSJ* **51**, 63.
3. **Calculated 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.
*cf.* Hannay *et al.*, *PRL***14**, 225 (1965).
$RbC_8$, $CsC_8$ : superconduct, but $T_c$ is much less than 0.1K.
$LiC_6$, $KC_{16}$(2nd stage), $KC_{24}$ (3rd stage) *etc.*: do not superconduct.



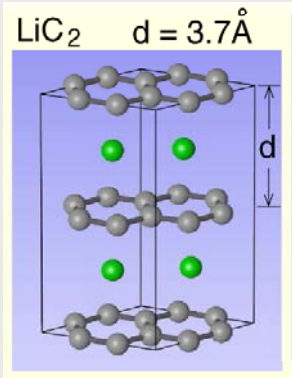

$T_c$ depends rather strongly on samples:

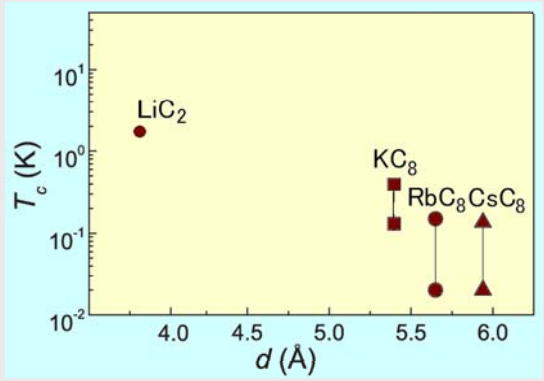
- $KC_8$: 0.08 - 0.55K (→ 0.15K)
- $RbC_8$: 0.023 - 0.151K (→ 0.026K)
- $CsC_8$: 0.02 - 0.135K



## Alkali Intercalated Graphite: 80s-90s

$LiC_2$: found to superconduct in 1989 with $T_c$=1.9K.
*cf.* Belash *et al.*, *SSC***69**, 921 (1989).
Some other superconductors with $T_c$ around 1K are also found in this class of materials in 80s and 90s.



## Alkaline-Earth Intercalated Graphite

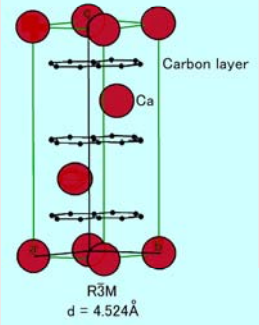
Breakthrough in 2005:

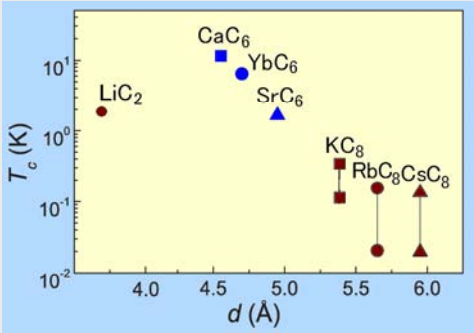
$CaC_6$: $T_c$ = 11.5K [Weller *et al.*, *Nature Phys.* ***1***, 39(2005); Emery et al., *PRL* ***95***, 087003(2005)]

up to 15.1K under pressures [Gauzzi *et al.*, *PRL* ***98***, 067002(2007)]

$YbC_6$: $T_c$ = 6.5K

$SrC_6$: $T_c$ = 6.5K [Kim *et al.*, *PRL* ***99***, 027001(2007)]

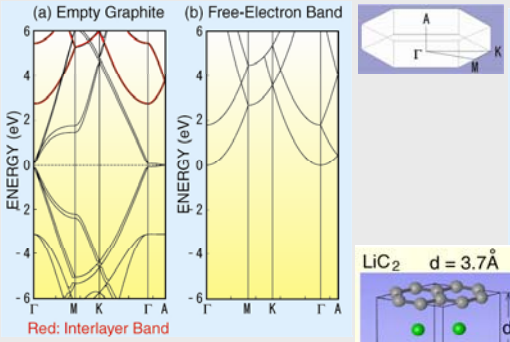


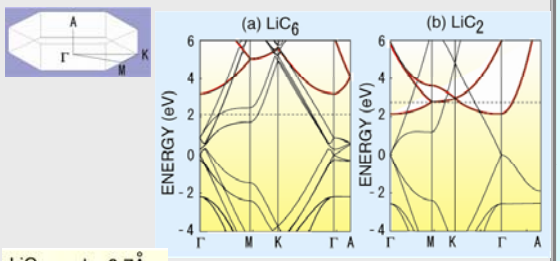



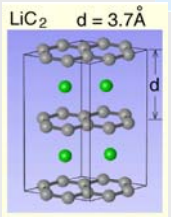



## Electronic Band Structure: $LiC_2$ and $LiC_6$

Band calculation:
$LiC_6$, $LiC_2$:[Csanyi *et al.*, *Nature Phys.* ***1***, 42 (2005)]



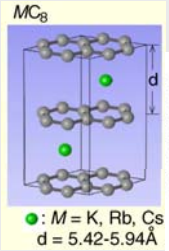

Interlayer band
→ 3D electron gas

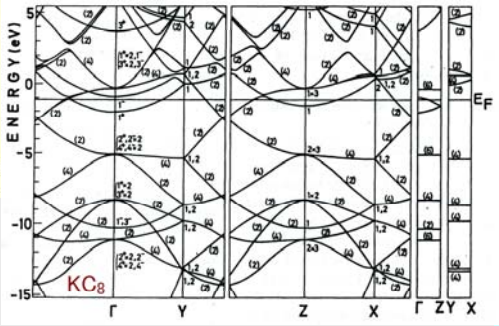
The interlayer band is occupied in $LiC_2$, but not in $LiC_6$.

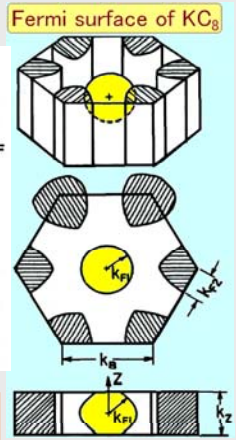


## Electronic Band Structure: $KC_8$

Band calculation:
$KC_8$:[Ohno *et al.*, *JPSJ* ***47***, 1125(1979); Wang *et al.*, *PRB* ***44***, 8294(1991)]




Coexistence of 2D and 3D electrons



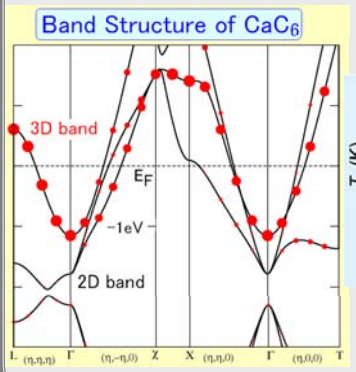
## Electronic Band Structure: $CaC_6$, $YbC_6$

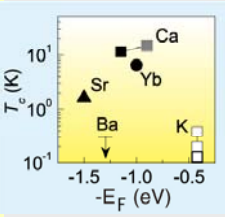
$CaC_6$, $YbC_6$:[Mazin,*PRL* ***95***, 227001 (2005); Calandra & Mauri,*PRL* ***95***, 237002 (2005)]

Important common features

(1) 2D- and 3D-electron systems coexist.

(2) Only 3D electrons in the interlayer band superconduct.

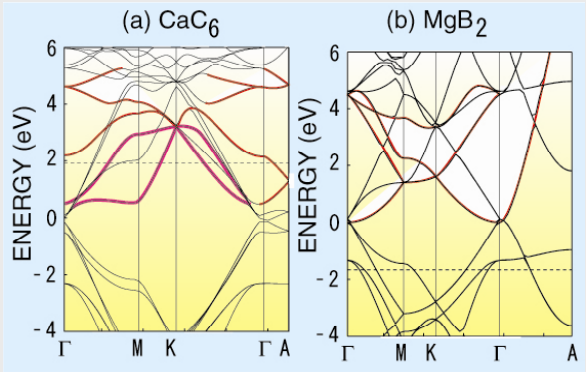



| GIC | doping | d | 3D electron | $T_c$ |
|---|---|---|---|---|
| graphite | 0 | 3.35Å | no | – |
| $C_6Li$ | 1/6 | 3.7Å | no | – |
| $C_3Li$ | 1/3 | 3.7Å | no | – |
| $C_2Li$ | 1/2 | 3.7Å | yes | 1.9K |
| $C_{16}K$ | 1/16 | 5.2Å | no | – |
| $C_8K$ | 1/8 | 5.2Å | yes | 0.14K |
| $C_6Ca$ | 1/3 | 4.6Å | yes | 11.5K |
| $C_6Yb$ | 1/3 | 4.7Å | yes | 6.5K |
| $C_6Ba$ | 1/3 | 5.25Å | yes | ? |

The interlayer band is much modified due to the mixing with the d bands of Ca atom. → $m^* \sim 3m_e$

## Comparison with $MgB_2$




In $MgB_2$, 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.



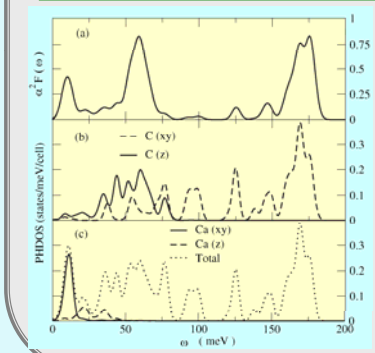
## Phonon Mechanism

Phonon mechanism of superconductivity for $CaC_6$ is proposed by calculating the Eliashberg function $\alpha^2F(\omega)$:

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 (α~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 λ is not properly treated.)

"Why is $T_c$ so much enhanced?"
→ Needs much more work!



## 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 $KC_8$ to $CaC_6$ 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: $MC_x$

This model was proposed already in 1982 for explaining superconductivity in $MC_8$ ($M$=K,Rb,Cs): YT, *JPSJ* ***51***, 63 (1982)

Model for $MC_x$ ($x$=2, 6, 8)

$M \rightarrow M^{+Z} + Ze^-$

Metal ion density: $n_M = \frac{4}{27^{1/2}a^2dx}$

($a$=1.419Å: C-C bond length)

$e^-$: f → localized on graphite layers (2D π-electrons)

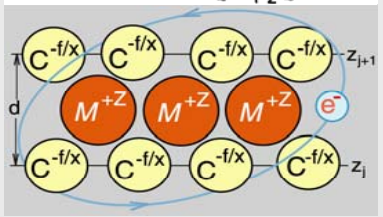
$e^-$: 1-f → occupy interlayer states (3D itinerant electrons)

3D electron density: $n_{3D} = Z(1-f)n_M$

3D electrons couple strongly with polar LO- and LA-phonons.

High-energy intralayer C modes will be neglected.

Description of the 2D electrons
wave function: $\exp(i\underset{\sim}{p}\underset{\sim}{r})f(z-z_j)$
$f(z) = \sqrt{\Lambda^3/2}\cdot z\exp(-\Lambda z/2)$, $(\Lambda^{-1} \ll d)$
linear dispersion: $\epsilon_{\underset{\sim}{p}} = v_{F2}|\underset{\sim}{p}|$




$$W^0(q,\omega) = \text{(p+q, p'-q; LA,LO; p, p')} = V^0(q)\frac{\omega_p(f)^2}{\omega^2-\omega_{LA}(f)^2} + V^0(q)\frac{\bar{\omega}_p(f)^2}{\omega^2-\omega_{LO}(f)^2}$$

where
$V^0(q) = \frac{4\pi e^2}{q^2}$, $\omega_p(f) = \sqrt{\frac{4\pi n_M e^2}{\bar{M}}z(1-f)}$, $\bar{\omega}_p(f) = \sqrt{\frac{4\pi n_M e^2}{\bar{m}}z\left(\frac{\bar{m}}{m_M}+f\frac{\bar{m}}{m_{C_x}}\right)}$
$(\bar{M} = m_M + m_{C_x}$, $1/\bar{m} = 1/m_M + 1/m_{C_x})$

# Hamiltonian for the Model

*cf.* YT, *JPSJ* ***51***, 63 (1982)

$$H=\sum_{\boldsymbol{p}\sigma}\varepsilon_{\boldsymbol{p}}c^{+}_{\boldsymbol{p}\sigma}c_{\boldsymbol{p}\sigma}+\sum_{iv}\sum_{\boldsymbol{p}\sigma}\varepsilon_{\boldsymbol{p}}a^{+}_{iv\boldsymbol{p}\sigma}a_{iv\boldsymbol{p}\sigma}+\sum_{\lambda}\sum_{\boldsymbol{k}}{\sum_{k_z}}'\omega_{\lambda}(\boldsymbol{K})b^{+}_{\lambda\boldsymbol{K}}b_{\lambda\boldsymbol{K}}+H_{\mathrm{el-el}}+H_{\mathrm{el-ph}}$$

$$H_{\mathrm{el-el}}=\frac{1}{2}\sum_{\boldsymbol{P}\boldsymbol{P}'}\sum_{\boldsymbol{Q}}\sum_{\sigma\sigma'}V^{0}(\boldsymbol{q},q_z)c^{+}_{\boldsymbol{P}+\boldsymbol{Q}\sigma}c^{+}_{\boldsymbol{P}'-\boldsymbol{Q}\sigma'}c_{\boldsymbol{P}'\sigma'}c_{\boldsymbol{P}\sigma}$$
$$+\sum_{\boldsymbol{p}\boldsymbol{p}'}\sum_{\boldsymbol{q}}\sum_{\substack{iv\\ \sigma\sigma'}}\sum_{j}{\sum_{k_z}}'V^{0}\left(\boldsymbol{q},k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)\mathrm{e}^{ik_zz_i}a^{+}_{iv\boldsymbol{p}+\boldsymbol{q}\sigma}c^{+}_{\boldsymbol{p}'-\boldsymbol{q},p_z'-k_z-(2\pi/d)j\sigma'}c_{\boldsymbol{p}'p_z'\sigma'}a_{iv\boldsymbol{p}\sigma}$$
$$+\frac{1}{2}\sum_{\boldsymbol{p}\boldsymbol{p}'}\sum_{\boldsymbol{q}}\sum_{ii'}\sum_{\substack{vv'\\ \sigma\sigma'}}\sum_{j}{\sum_{k_z}}'V^{0}\left(\boldsymbol{q},k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)^{2}\exp\{ik_z(z_i-z_{i'})\}\,a^{+}_{iv\boldsymbol{p}+\boldsymbol{q}\sigma}a^{+}_{i'v'\boldsymbol{p}'-\boldsymbol{q}\sigma'}a_{i'v'\boldsymbol{p}'\sigma'}a_{iv\boldsymbol{p}\sigma}$$

$$H_{\mathrm{el-ph}}=\sum_{\boldsymbol{P}}\sum_{\boldsymbol{k}}\sum_{\lambda\sigma}\sum_{j}{\sum_{k_z}}'g_{\lambda}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)c^{+}_{\boldsymbol{p}+\boldsymbol{k},p_z+k_z+(2\pi/d)j,\sigma}c_{\boldsymbol{P}\sigma}b_{\lambda\boldsymbol{K}}$$
$$+\sum_{i\lambda}\sum_{\sigma}\sum_{\boldsymbol{p}\boldsymbol{k}}{\sum_{k_z}}'g_{i\lambda}(\boldsymbol{k})a^{+}_{iv\boldsymbol{p}+\boldsymbol{k}\sigma}a_{iv\boldsymbol{p}\sigma}b_{\lambda\boldsymbol{k}}+\mathrm{c.c.}$$

with

$$g_{\lambda}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)=i\sqrt{V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)\Big/2\omega_{\lambda}(\boldsymbol{K})}\;G_{j\lambda}(\boldsymbol{K})$$

$$g_{i\lambda}(\boldsymbol{K})=i\,\mathrm{e}^{ik_zz_i}\sum_{j}F\left(k_z+\frac{2\pi}{d}j\right)\times\sqrt{V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)\Big/2\omega_{\lambda}(\boldsymbol{K})}\;G_{j\lambda}(\boldsymbol{K})$$

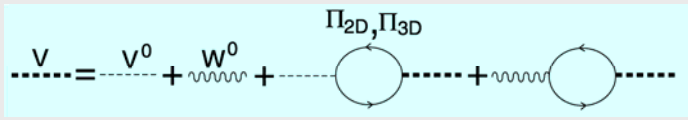
$$G_{j,LA}(\boldsymbol{K})=\omega_{p}\sqrt{V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)\Big/4\pi e^{2}(k^{2}+k_z^{2})}\times\left\{(-1)^{j}\left[k^{2}+k_z\left(k_z+\frac{2\pi}{d}j\right)\right]-fk_z\left(k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)\right\}$$

$$G_{j,LO}(\boldsymbol{K})=\bar{\omega}_{p}\sqrt{V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)\Big/4\pi e^{2}(k^{2}+k_z^{2})}\times\left\{(-1)^{j}\frac{\bar{m}}{m_{\mathrm{M}}}\left[k^{2}+k_z\left(k_z+\frac{2\pi}{d}j\right)\right]+f\frac{\bar{m}}{m_{\mathrm{C_X}}}k_z\left(k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)\right\}$$



# Effective Interaction

The electron-electron effective interaction is calculated in the RPA with taking the layer structure into account, amounting to the $G_0W_0$ (one-shot GW) approximation.




$$V(\boldsymbol{Q},i\Omega)=\frac{V^{0}(\boldsymbol{k},q_z)}{\varepsilon_{j}(\boldsymbol{K},i\Omega)}\{1-\Pi_{2D}(\boldsymbol{k},i\Omega)U_{j}(\boldsymbol{K},i\Omega)/[1+\Pi_{2D}(\boldsymbol{k},i\Omega)\sum_{j'}U_{j'}(\boldsymbol{K},i\Omega)]\}$$

$$V^{0}(\boldsymbol{q},q_z)=4\pi e^{2}/(\varepsilon_{\infty}^{\perp}\boldsymbol{q}^{2}+\varepsilon_{\infty}^{/\!/}q_z^{2}),\quad E_{j}(\boldsymbol{K},\omega)=1+\sum_{\lambda}\frac{G_{j\lambda}(\boldsymbol{K})^{2}}{\omega^{2}-\omega_{\lambda}(\boldsymbol{K})^{2}},\quad (\lambda=\mathrm{TA\ or\ TO})$$

$$\varepsilon_{j}(\boldsymbol{K},i\Omega)=E_{j}^{-1}(\boldsymbol{K},i\Omega)+V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi j}{d}\right)\Pi_{3D}(\boldsymbol{K}_{j},i\Omega)$$

$$U_{j}(\boldsymbol{K},i\Omega)=V^{0}\left(\boldsymbol{k},k_z+\frac{2\pi j}{d}\right)F\left(k_z+\frac{2\pi j}{d}\right)^{2}\Big/\varepsilon_{j}(\boldsymbol{K},i\Omega)$$

$$F(q_z)=\int\mathrm{d}z\,f^{2}(z)\,\mathrm{e}^{iq_zz}=\{1-3(q_z/\Lambda)^{2}\}/\{1+(q_z/\Lambda)^{2}\}^{3}$$

No ambiguity in treating the screening effect!



# Gap Equation

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

Anomalous Green's Function: $F(\mathbf{p},i\omega_p)=-\int_0^{1/T}d\tau e^{i\omega_p\tau}\langle T_\tau c_{\mathbf{p}\uparrow}(\tau)c_{-\mathbf{p}\downarrow}\rangle$

$$F(\mathbf{p},i\omega_p)=-G(\mathbf{p},i\omega_p)G(-\mathbf{p},-i\omega_p)\,T\sum_{\omega_{p'}}\sum_{\mathbf{p}'}\tilde{I}(\mathbf{p},\mathbf{p}';i\omega_p,i\omega_{p'})F(\mathbf{p}',i\omega_{p'})$$

← Exact gap equation

$G_0W_0$ approximation $\quad G\to G_0\quad \tilde{I}\to V$

$$\Delta(\mathbf{p})\equiv 2|\varepsilon_{\mathbf{p}}|\int_0^{\infty}\frac{d\omega}{\pi}\mathrm{Im}\,F^{R}(\mathbf{p},\omega)$$

At $T=T_c$

$$\Delta(\mathbf{p})=-\sum_{\mathbf{p}'}\frac{\Delta(\mathbf{p}')}{2\varepsilon_{\mathbf{p}'}}\tanh\frac{\varepsilon_{\mathbf{p}'}}{2T_c}V_{\mathbf{p},\mathbf{p}'}$$

← The energy variable is integrated out.

Pairing Interaction:

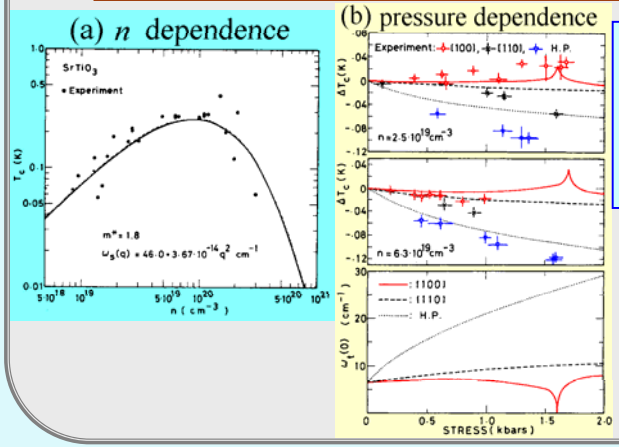
$$V_{\mathbf{p},\mathbf{p}'}=V^{0}(\mathbf{p}\text{-}\mathbf{p}')+\int_0^{\infty}\frac{2}{\pi}d\Omega\frac{\mathrm{Im}\,V^{R}(\mathbf{p}\text{-}\mathbf{p}',\Omega)}{\Omega+|\varepsilon_{\mathbf{p}}|+|\varepsilon_{\mathbf{p}'}|}=\int_0^{\infty}\frac{2}{\pi}d\Omega\frac{|\varepsilon_{\mathbf{p}}|+|\varepsilon_{\mathbf{p}'}|}{\Omega^{2}+(|\varepsilon_{\mathbf{p}}|+|\varepsilon_{\mathbf{p}'}|)^{2}}V(\mathbf{p}\text{-}\mathbf{p}',i\Omega)$$

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)
→ Possibility of a negative $\mu^*$ in the low-density electron gas ("Plasmon mechanism" of superconductivity)
Its successful application to polar semiconductors such as $SrTiO_3$ is explained in: YT, *JPSJ* ***49***, 1267 (1980).




Stress-induced ferroelectric transition
→ softening the polar optic mode
→ bringing about superconductivity

In $SrTiO_3$, $n\sim10^{20}\mathrm{cm}^{-3}$, while in $CaC_6$, $n\sim2\times10^{22}\mathrm{cm}^{-3}$, which is not in the region of negative $\mu^*$.

## Gap Anisotropy

Although the one-electron dispersion is isotropic, the effective interaction is anisotropic, leading to an anisotropic gap equation.

Legendre expansion

$$\Delta(P)=\sum_l \sqrt{\frac{2l+1}{4\pi}}\Delta_l(\omega)P_l(\cos\theta) \qquad \Delta_l(\omega)=-\int_{-\varepsilon_F}^{\infty}\frac{d\omega'}{2\omega'}\tanh\frac{\omega'}{2T_c}\sum_{l'}\Delta_{l'}(\omega')K_{ll'}(\omega,\omega')$$

Kernel:

$$K_{ll'}(\omega,\omega')=\frac{m^*|P'|}{16\pi^3}\sqrt{(2l+1)(2l'+1)}\int_0^{\pi}\sin\theta d\theta\int_0^{\pi}\sin\theta' d\theta'\int_0^{2\pi}d\phi\,P_l(\cos\theta)P_{l'}(\cos\theta')\int_0^{\infty}\frac{2}{\pi}d\Omega\frac{|\omega|+|\omega'|}{\Omega^2+(|\omega|+|\omega'|)^2}V(P-P';i\Omega)$$

It turns out that the effect of anisotropy on $T_c$ is not so important; $T_c$ in the s-wave approximation is enough in most cases, but this does not mean that the gap function itself is almost isotropic.



## 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 number $f$, 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)

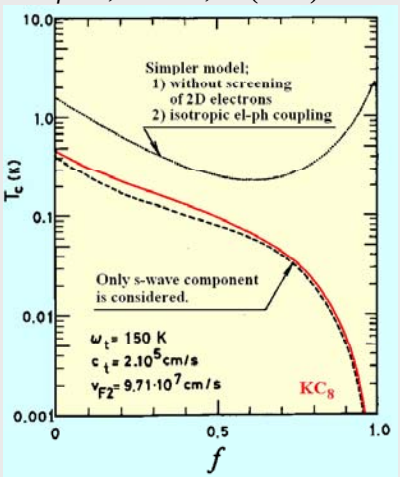
| | K (Alkali GICs) | Ca (Alkaline-earth GICs) |
|---|---|---|
| $Z$ | 1 | 2 |
| $d$ | ~ 5.5A | ~ 4.5A (higher density) |
| $f$ | ~ 0.6 | ~ 0.15 |
| $m^*$ | ~ $m_e$ (s-like electron) | ~ $3m_e$ (d-like electron) |

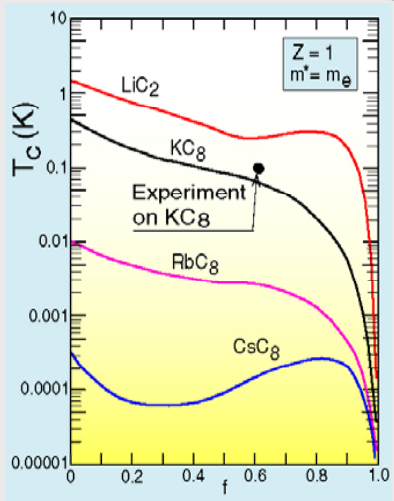
*cf.* $m_M$ (A=40.1) for Ca is about the same as that of K (A=39.1).



## $T_c$ for Alkali-Doped GICs

*cf.* YT, *JPSJ* ***51***, 63 (1982)



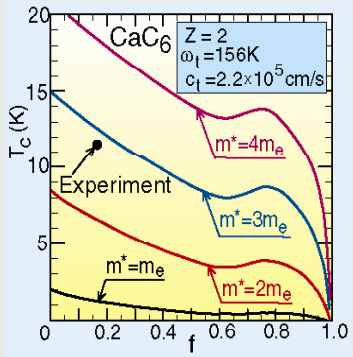

(1) For $KC_8$, $RbC_8$, $CsC_8$, the results are just the same as those in 1982.

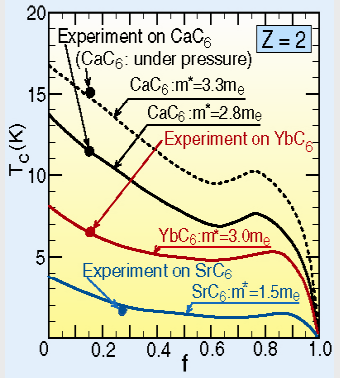
(2) For $LiC_2$, our result is of the same order of the experimental result.



## $T_c$ for Alkaline-Earth-Doped GICs

YT, *JPSJ* ***78***, 013703 (2009)




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

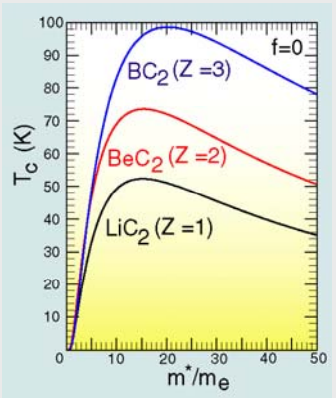
(1) Smaller $f$ is favorable, because the screening effect of 2D electrons is weaker.

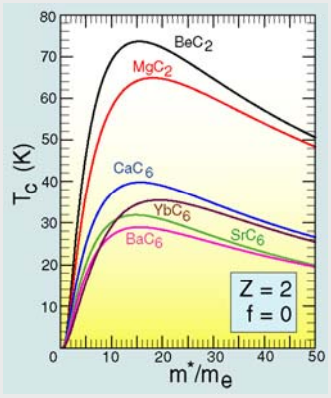
(2) Doubling $Z$ enhances $T_c$ by a factor of ten.

(3) Tripling $m^*$ enhances $T_c$ by another factor of ten.

(4) "Isotope effect": Ca (A=40.1) vs Yb (A=173.0) → $\alpha \sim 0.5$

## 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

$1^0$ A successful model is explained for superconductivity in GICs with $T_c$ ranging over three orders of magnitude.

$2^0$ A very important effect of the effective mass $m^*$ of the 3D electrons on $T_c$ is revealed.

$3^0$ 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.