On the First-Principles Determination of the Superconducting Transition Temperature

Yasutami Takada
Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: takada@issp.u-tokyo.ac.jp

One of the ultimate goals in condensed matter theory is to make a reliable prediction of the superconducting transition temperature T_c only through the information on constituent elements of a superconductor in consideration. A less ambitious yet very important goal is to make an accurate evaluation of T_c directly from a microscopic (yet model) Hamiltonian pertinent to the superconductor. If we could find the dependence of T_c on the parameters specifying the model Hamiltonian, we could obtain an insight into the mechanism of superconductivity or the competition between attractive and repulsive interactions between electrons. Accumulation of such basic information would pave the way to the synthesis of a room-temperature superconductor, a big dream in materials science.

From this perspective, a critical review of the theories for quantitative calculations of T_c from first principles is given in my talk. In view of the importance to avoid employing the phenomenological parameters such as the Coulomb pseudopotential μ^* in describing the effect of the Coulomb repulsion on the Cooper-pair formation, I focus on the density functional theory for superconductors (SCDFT) as well as the G_0W_0 approximation to the exact theory in the Green's-function approach. I give some concrete results of T_c for actual superconductors including the pseudoferroelectric *n*-type semiconducting $SrTiO_3$ [1] and the alkali- and alkaline-earth-intercalated graphite compounds [2-4] with paying special attention to the surprising similarity in the gap equation obtained in each theory, implying a deep implicit interconnection between the two theories, in spite of the large difference in their basic theoretical frameworks [5,6].

References

[1] Y. Takada, J. Phys. Soc. Jpn. **49**, 1267 (1980).
[2] Y. Takada, J. Phys. Soc. Jpn. **51**, 63 (1982).
[3] Y. Takada, J. Phys. Soc. Jpn. **78**, 013703 (2009).
[4] Y. Takada, Reference Module in Materials Science and Materials Engineering (Elsevier, 2016) doi: 10.1016/B978-0-12-803581-8.00774-8].
[5] Y. Takada, in "Carbon-based superconductors: Toward high-T_c superconductivity", edited by J. Haruyama (Pan Stanford, Singapore, 2015), pp. 193-230; ISBN: 978-981-4303-30-9 (Hardcover), 978-981-4303-31-6 (eBook).
[6] Y. Takada, Molecular Physics **114**, 1041 (2016) [doi:10.1080/00268976.2015.1131860].

Seminar @ Academia Sinica

On the First-Principles Determination of the Superconducting Transition Temperature

Yasutami Takada

The Institute for Solid State Physics, The University of Tokyo
5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581

takada@issp.u-tokyo.ac.jp

505B Meeting Room, 5F, IRBST
Research Center for Applied Sciences, Academia Sinica, Taipei
14:00-16:00, Wednesday, 21 December 2016

cf. YT, Reference Module in Materials Science and Materials Engineering (Elsevier, 2016) doi: 10.1016/B978-0-12-803581-8.00774-8.
YT, Molecular Physics **114**, 1041 (2016).

Outline

Polar Crystals

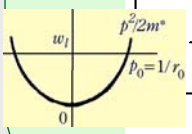
◎ Late 70's: High-T_c superconductivity in CuCl and CdS?

→ Investigate the possibility of high-T_c superconductivity in doped polar crystals with low carrier density in terms of bipolaron Bose-Einstein condensation (BEC)

← A research subject given by Prof. Al Overhauser (1925-2011).

Many-electron Fröhlich polaron model

$$H=\sum_{\mathbf{p}\sigma}\frac{p^2}{2m^*}c^+_{\mathbf{p}\sigma}c_{\mathbf{p}\sigma}+\frac{1}{2}\sum_{\mathbf{q}\neq\mathbf{0}}\sum_{\mathbf{p}\sigma}\sum_{\mathbf{p}'\sigma'}\frac{4\pi e^2}{\varepsilon_\infty q^2}c^+_{\mathbf{p}+\mathbf{q}\sigma}c^+_{\mathbf{p}'-\mathbf{q}\sigma'}c_{\mathbf{p}'\sigma'}c_{\mathbf{p}\sigma}$$
$$+\sum_{\mathbf{p}\sigma}\sum_{\mathbf{q}\neq\mathbf{0}}g_{\mathbf{q}}c^+_{\mathbf{p}+\mathbf{q}\sigma}c_{\mathbf{p}\sigma}(b_{\mathbf{q}}-b^+_{-\mathbf{q}})+\sum_{\mathbf{q}}\omega_l\left(b^+_{\mathbf{q}}b_{\mathbf{q}}+\frac{1}{2}\right)$$



$$g_{\mathbf{q}}=\frac{i}{q}\sqrt{\frac{4\pi e^2\omega_l}{2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)},\quad \alpha\equiv\frac{1}{2}\frac{e^2}{r_0\omega_l}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right),r_0=\frac{1}{\sqrt{2m^*\omega_l}}$$

Fröhlich Polaron Model

◎ One-electron problem→Fröhlich polaron $\frac{p^2}{2m^*}\rightarrow-\alpha\omega_l+\frac{p^2}{2m^*(1+\alpha/6)}$

→ Diagrammatic QMC: Mishchenko et al. , PRB**62**, 6317 (2000).

◎ Two-electron problem → Interaction between electrons

$$V^{\mathrm{R}}(\boldsymbol{q},\omega)=\frac{4\pi e^2}{\boldsymbol{q}^2\varepsilon^{\mathrm{R}}(\boldsymbol{q},\omega)}$$

$$\varepsilon^{\mathrm{R}}(\boldsymbol{q},\omega)=\varepsilon_\infty+[\varepsilon_0(\boldsymbol{q})-\varepsilon_\infty]\frac{\omega_t(\boldsymbol{q})^2}{\omega_t(\boldsymbol{q})^2-\omega^2-i0^+}\quad\text{with}\quad\varepsilon_0(\boldsymbol{q})=\varepsilon_0\frac{\omega_t(0)^2}{\omega_t(\boldsymbol{q})^2}$$

$$\omega_l=\sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}}\,\omega_t(0):\text{Lyddane-Sachs-Teller}$$

→ Bipolaron (i.e., preformed pair) is not constructed unless $\alpha\gg1$
YT, PRB**26**, 1223(1983); Hiramoto-Toyozawa, JPSJ, 1985

"Bipolaron high-T_c superconductivity" is not expected to occur.

◎ Many-electron problem

$$\varepsilon^{\mathrm{R}}(\boldsymbol{q},\omega)=\varepsilon_\infty+\frac{4\pi e^2}{\boldsymbol{q}^2}\Pi^{\mathrm{R}}(\boldsymbol{q},\omega)+[\varepsilon_0(\boldsymbol{q})-\varepsilon_\infty]\frac{\omega_t(\boldsymbol{q})^2}{\omega_t(\boldsymbol{q})^2-\omega^2-i0^+}$$

→ Cooper pairs can be formed even for small α, but how about T_c?

General Model for Electron-Phonon System

Hamiltonian

$$\mathcal{H}_{ep} = \sum_{p\sigma}\xi_p c^\dagger_{p\sigma}c_{p\sigma} + \frac{1}{2}\sum_{q\neq 0}\sum_{p\sigma}\sum_{p'\sigma'} V_c(q)c^\dagger_{p+q\sigma}c^\dagger_{p'-q\sigma'}c_{p'\sigma'}c_{p\sigma} + \sum_{q\lambda}\omega_{q\lambda}b^\dagger_{q\lambda}b_{q\lambda} + \sum_{p\sigma}\sum_{q\neq 0\lambda} g_\lambda(q)c^\dagger_{p+q\sigma}c_{p\sigma}(b_{q\lambda}+b^\dagger_{-q\lambda})$$

$$V_c(q) \equiv 4\pi e^2/\varepsilon_\infty q^2 \quad (\varepsilon_\infty : \text{optical dielectric constant})$$

Nambu Representation

$$\Psi_p = \begin{pmatrix} c_{p\uparrow} \\ c^\dagger_{-p\downarrow} \end{pmatrix}, \quad \Psi^\dagger_p = (c^\dagger_{p\uparrow}\ c_{-p\downarrow})$$

←Singlet pairing

$$\mathcal{H}_{ep} = \sum_p \xi_p \Psi^\dagger_p \tau_3 \Psi_p + \frac{1}{2}\sum_{q\neq 0}\sum_{p,p'} V_c(q)(\Psi^\dagger_{p+q}\tau_3\Psi_p)(\Psi^\dagger_{p'-q}\tau_3\Psi_{p'}) + \sum_{q\lambda}\omega_{q\lambda}b^\dagger_{q\lambda}b_{q\lambda} + \sum_p\sum_{q\neq 0\lambda} g_\lambda(q)\Psi^\dagger_{p+q}\tau_3\Psi_p(b_{q\lambda}+b^\dagger_{-q\lambda})$$

Green's Function

$$G_p(\tau) \equiv -\langle T_\tau \Psi_p(\tau)\Psi^\dagger_p\rangle = \begin{pmatrix} -\langle T_\tau c_{p\uparrow}(\tau)c^\dagger_{p\uparrow}\rangle & -\langle T_\tau c_{p\uparrow}(\tau)c_{-p\downarrow}\rangle \\ -\langle T_\tau c^\dagger_{-p\downarrow}(\tau)c^\dagger_{p\uparrow}\rangle & -\langle T_\tau c^\dagger_{-p\downarrow}(\tau)c_{-p\downarrow}\rangle \end{pmatrix}$$

$$G_p(i\omega_p) = -\int_0^{1/T} d\tau\, e^{i\omega_p\tau}\langle T_\tau \Psi_p(\tau)\Psi^\dagger_p\rangle$$

Off-diagonal part→ Anomalous Green's Function: $F(\boldsymbol{p},i\omega_p)$

Exact Self-Energy

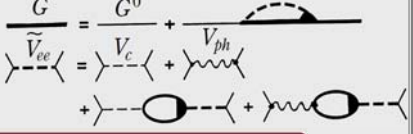
Formally exact equation to determine the self-energy

$$\Sigma_p(i\omega_p) = -T\sum_{\omega_q}\sum_{q\neq 0}\tau_3 G_{p+q}(i\omega_p+i\omega_q)\Gamma_{p+q,p}(i\omega_p+i\omega_q, i\omega_p)\,\tilde{V}_{ee}(q, i\omega_q)$$

Effective electron-electron interaction

$$\tilde{V}_{ee}(q, i\omega_q) \equiv \frac{V_{ee}(q, i\omega_q)}{1 + V_{ee}(q, i\omega_q)\Pi(q, i\omega_q)}$$

$G^{-1} = G_0^{-1} - \Sigma$



Bare electron-electron interaction

$$V_{ee}(q, i\omega_q) = V_c(q) + \sum_\lambda |g_\lambda(q)|^2 \frac{2\omega_{q\lambda}}{(i\omega_q)^2 - \omega^2_{q\lambda}} \equiv V_c(q) + V_{ph}(q, i\omega_q)$$

Polarization function

$$\Pi(q, i\omega_q) = -T\sum_{\omega_p}\sum_{p}\mathrm{Tr}\left[\tau_3 G_p(i\omega_p)\Gamma_{p,p+q}(i\omega_p, i\omega_p+i\omega_q)G_{p+q}(i\omega_p+i\omega_q)\right]$$

Direct extension of the Hedin's exact set of equations !

Eliashberg Theory

Basic assumption: $\Theta_D/E_F \ll 1$

(1) Migdal Thorem: $\Gamma_{\boldsymbol{p}+\boldsymbol{q},\boldsymbol{p}}(i\omega_p + i\omega_q, i\omega_p) = \tau_3$

(2) Separation between phonon-exchange & Coulomb parts

$$\tilde{V}_{ee}(\boldsymbol{q}, i\omega_q) = \frac{V_c(q)}{1+V_c(q)\Pi(\boldsymbol{q}, i\omega_q)} + \frac{1}{[1+V_c(q)\Pi(\boldsymbol{q}, i\omega_q)]^2} \frac{V_{ph}(\boldsymbol{q}, i\omega_q)}{1+\frac{V_{ph}(\boldsymbol{q}, i\omega_q)\Pi(\boldsymbol{q}, i\omega_q)}{1+V_c(q)\Pi(\boldsymbol{q}, i\omega_q)}}$$

neglect for a while ↑

$\Pi(\boldsymbol{q}, i\omega_q) \rightarrow \Pi(\boldsymbol{q}, 0)$: perfect screening ↑

(3) Introduction of the Eliashberg function

$$\tilde{V}_{ee}(i\omega_q) = \frac{1}{N(0)} \int_0^\infty d\Omega\, \alpha^2 F(\Omega) \frac{2\Omega}{(i\omega_q)^2 - \Omega^2}$$

$N(0)$: Density of states per one spin at E_F

(4) Restriction to the Fermi surface & electron-hole symmetry

$$\Sigma_{\boldsymbol{p}}(i\omega_p) = [1 - Z_{\boldsymbol{p}}(i\omega_p)] i\omega_p \tau_0 + \chi_{\boldsymbol{p}}(i\omega_p)\tau_3 + \phi_{\boldsymbol{p}}(i\omega_p)\tau_1$$
$$\xrightarrow[\boldsymbol{p}=\boldsymbol{p}_F]{} [1 - Z(i\omega_p)] i\omega_p \tau_0 + \phi(i\omega_p)\tau_1$$

Renormalization Function and Gap Function

(1) Equation to determine the Renormalization Function

$$Z(i\omega_p) = 1 + \frac{\pi}{\omega_p} T \sum_{\omega_{p'}} \lambda(p'-p)\, \eta_{p'}(\omega_c)$$

(2) Gap Equation at $T = T_c$

$$\Delta(i\omega_p) = \frac{\pi}{Z(i\omega_p)} T \sum_{\omega_{p'}} \lambda(p'-p) \frac{\Delta(i\omega_{p'})}{\omega_{p'}} \eta_{p'}(\omega_c) \qquad \Delta(i\omega_p) \equiv \frac{\phi(i\omega_p)}{Z(i\omega_p)}$$

Function $\lambda(n)$ with n: an integer

$$\lambda(n) = \int_0^\infty d\Omega\, \alpha^2 F(\Omega) \frac{2\Omega}{\Omega^2 + (2\pi T n)^2}$$

Cutoff function $\eta_p(\omega_c)$ with ω_c of the order of Θ_D

$$\eta_p(\omega_c) = \frac{2}{\pi} \tan^{-1}\left(\frac{\omega_c}{Z(i\omega_p)\omega_p}\right)$$

Inclusion of Coulomb Repulsion

(1) Equation to determine the Renormalization Function

$$Z(i\omega_p)=1+\frac{\pi}{\omega_p}T\sum_{\omega_{p'}}\lambda(p'-p)\,\eta_{p'}(\omega_c)$$

← Invariant!

(2) Gap Equation

$$\Delta(i\omega_p)=\frac{\pi}{Z(i\omega_p)}T\sum_{\omega_{p'}}\frac{\Delta(i\omega_{p'})}{\omega_{p'}}[\lambda(p'-p)-\mu^*]\eta_{p'}(\omega_c)$$

← Revised

Coulomb pseudopotential

$$\mu^*=\frac{\mu_c}{1+\mu_c\ln(E_F/\omega_c)} \qquad \mu_c=N(0)\left\langle\frac{V_c(q)}{1+V_c(q)\Pi(q,0)}\right\rangle$$

$V_c(q)\propto q^{-2}$, $\Pi(\mathbf{0},0)=2N(0)$ → $\mu_c\approx N(0)/\Pi(\mathbf{0},0)\approx 0.5$

$E_F/\omega_c=0.01-0.001$ → $\mu^*=0.11-0.15$

Eliashberg Function

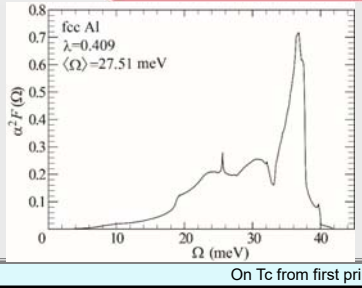
Method for *ab-initio* calculation of $\alpha^2F(\Omega)$

$$\alpha^2F(\Omega)=\frac{\sum_{n\mathbf{k}}\sum_{n'\mathbf{k}'}\sum_{\lambda}|g_\lambda(n'\mathbf{k}';n\mathbf{k})|^2\delta(\Omega-\omega_{\mathbf{k}'-\mathbf{k}\lambda})\delta(\xi_{n\mathbf{k}})\delta(\xi_{n'\mathbf{k}'})}{\sum_{n\mathbf{k}}\delta(\xi_{n\mathbf{k}})}$$

$\gamma_{\mathbf{q}\lambda}$: HWHM for phonon $\mathbf{q}\lambda$

$$\gamma_{\mathbf{q}\lambda}=2\pi\sum_{nn'\mathbf{k}'}|g_\lambda(n'\mathbf{k}';n\mathbf{k})|^2[f(\xi_{n\mathbf{k}})-f(\xi_{n\mathbf{k}}+\omega_{\mathbf{q}\lambda})]\delta(\xi_{n'\mathbf{k}'}-\xi_{n\mathbf{k}}-\omega_{\mathbf{q}\lambda})$$
$$\approx 2\pi\omega_{\mathbf{q}\lambda}\sum_{nn'\mathbf{k}'}|g_\lambda(n'\mathbf{k}';n\mathbf{k})|^2\delta(\xi_{n\mathbf{k}})\delta(\xi_{n'\mathbf{k}'})$$

Allen's formula $\alpha^2F(\Omega)=\frac{1}{2\pi N(0)}\sum_{\mathbf{q}\lambda}\frac{\gamma_{\mathbf{q}\lambda}}{\omega_{\mathbf{q}\lambda}}\delta(\Omega-\omega_{\mathbf{q}\lambda})$

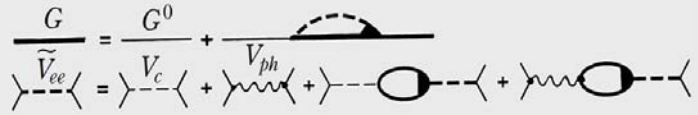


Package: Quantum Espresso
k-points : 48x48x48
q(=***k'***-***k***)-points : 16x16x16

$$\langle\Omega\rangle=\frac{2}{\lambda}\int_0^\infty d\Omega\,\alpha^2F(\Omega)$$

Consideration on the Ward Identity

$$\Sigma_{\boldsymbol{p}}(i\omega_p) = -T\sum_{\omega_q}\sum_{\boldsymbol{q}\neq\boldsymbol{0}} \tau_3 G_{\boldsymbol{p}+\boldsymbol{q}}(i\omega_p+i\omega_q)\Gamma_{\boldsymbol{p}+\boldsymbol{q},\boldsymbol{p}}(i\omega_p+i\omega_q, i\omega_p)\,\tilde{V}_{ee}(\boldsymbol{q}, i\omega_q)$$



Include Γ in terms of GWΓ theory for the normal state

↖ YT, PRL**87**, 226402 (2001).

Ward identity

$$i\omega_q\Gamma_{\boldsymbol{p}+\boldsymbol{q},\boldsymbol{p}}(i\omega_p+i\omega_q,i\omega_p) - \boldsymbol{q}\cdot\boldsymbol{\Gamma}_{\boldsymbol{p}+\boldsymbol{q},\boldsymbol{p}}(i\omega_p+i\omega_q,i\omega_p) = G_{\boldsymbol{p}+\boldsymbol{q}}(i\omega_p+i\omega_q)^{-1}\tau_3 - \tau_3 G_{\boldsymbol{p}}(i\omega_p)^{-1}$$

In accordance with the Eliashberg theory, after averaging over $\boldsymbol{p}$ dependence, we obtain

$$\Gamma(i\omega_p', i\omega_p) = \frac{\omega_{p'}Z(i\omega_{p'}) - \omega_p Z(i\omega_p)}{\omega_{p'} - \omega_p}\tau_3$$

← GISC scheme: YT, J. Phys. Chem. Solids**54**, 1779 (1993).

Comments will be given later on (1) case of $\omega_{p'}=\omega_p$ and (2) consideration on the effects of Anderson-Bogoliubov-Nambu-Goldstone & Higgs-Anderson modes.

Gap equations in GISC & G_0W_0

YT, J. Phys. Chem. Solids **54**, 1779 (1993)

Gauge-Invariant Self-Consistent (GISC) determination of $Z(i\omega_p)$

$$Z(i\omega_p) = 1 + \frac{\pi}{\omega_p}T\sum_{\omega_{p'}}\lambda(p'-p)\frac{\omega_{p'}Z(i\omega_{p'}) - \omega_p Z(i\omega_p)}{\omega_{p'}-\omega_p}\eta_{p'}(\omega_c)$$

Gap equation in GISC

$$\Delta(i\omega_p) = \frac{\pi}{Z(\omega_p)}T\sum_{\omega_{p'}}\frac{\Delta(i\omega_{p'})}{\omega_{p'}}[\lambda(p'-p)-\mu^*]\frac{\omega_{p'}Z(i\omega_{p'}) - \omega_p Z(i\omega_p)}{\omega_{p'}-\omega_p}\eta_{p'}(\omega_c)$$

Gap equation in G_0W_0 in which we take $Z(i\omega_p)=1$.

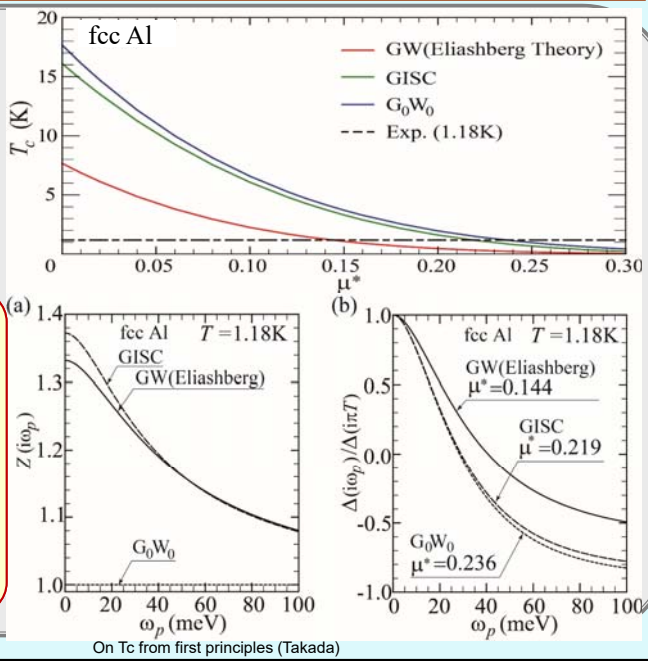
$$\Delta(i\omega_p) = \pi T\sum_{\omega_{p'}}\frac{\Delta(i\omega_{p'})}{\omega_{p'}}(\lambda(p'-p)-\mu^*)\eta_{p'}(\omega_c)$$

Comparison of T_c for Al among Three Schemes

Plot of T_c as a function of μ^* with $\lambda=0.409$

YT, Mol. Phys. **114**, 1041 (2016).

Conclusion
(1) T_c & Δ:
GISC ≈ G_0W_0 ≠ GW (Eliashberg)
(2) Z :
GISC ≈ GW (Eliashberg) ≠ G_0W_0



Comments

(1) What is the actual meaning of Migdal's theorem?
In the calculation of T_c, if all the vertex corrections are neglected, we should neglect all the self-energy correction as well, in order to satisfy the Ward identity.

(2) Polaron effect
The Ward identity determines the vertex function for $\omega_{p'} \neq \omega_p$ as

$$\Gamma(i\omega'_p, i\omega_p) = \frac{\omega_{p'} Z(i\omega_{p'}) - \omega_p Z(i\omega_p)}{\omega_{p'} - \omega_p}\tau_3$$

but it is useless for $\omega_{p'} = \omega_p$; instead, it is known as $\Gamma=[1-\delta\Sigma/\delta\mu]\tau_3$.
If the polaron effect is large, it is much different from Γ in the limit of $\omega_{p'} \to \omega_p$.
cf. YT & T. Higuchi, PRB**52**, 12720 (1995).

(3) Effect of Anderson-Bogoliubov-Nambu-Goldstone mode on T_c

$$(i\omega_{p'} - i\omega_p)\Gamma(i\omega_{p'}, i\omega_p) = [i\omega_{p'} Z(i\omega_{p'}) - i\omega_p Z(i\omega_p)]\tau_3 + [\phi(i\omega_{p'}) + \phi(i\omega_p)]i\tau_2$$

◎ Amplitude mode (Higgs mode) does not change T_c;
cf. T. Gherghetta & Y. Nambu, PRB**49**, 740 (1994).
◎ Phase mode, the energy scale of which is that of the plasmon, decreases T_c;
cf. YT, J. Phys. Chem. Solids **54**, 1779 (1993).

Gap Equation in G_0W_0 Approximation

Derive a gap equation in G_0W_0 in which $Z_{\boldsymbol{p}}(i\omega_p)=1$, $\chi_{\boldsymbol{p}}(i\omega_p)=0$.
cf. YT, JPSJ**45**, 786 (1978); JPSJ**49**, 1267 (1980).

At $T=T_c$,
$$\phi_{\boldsymbol{p}}(i\omega_p) = T\sum_{\omega_{p'}}\sum_{\boldsymbol{p}'\neq\boldsymbol{p}} \frac{\phi_{\boldsymbol{p}'}(i\omega_{p'})}{(i\omega_{p'})^2-\xi_{\boldsymbol{p}'}^2}\tilde{V}_{ee}(\boldsymbol{p}-\boldsymbol{p}', i\omega_p-i\omega_{p'})$$

Analytic continuation: $i\omega_p \to \omega+i0^+,\ \phi_{\boldsymbol{p}}(i\omega_p)\to\phi_{\boldsymbol{p}}^R(\omega)$

$$\phi_{\boldsymbol{p}}^R(\omega)=\int_0^\infty\frac{d\omega'}{\pi}\sum_{\boldsymbol{p}'}\mathrm{Im}\left[\frac{\phi_{\boldsymbol{p}'}^R(\omega')}{\omega'^2-\xi_{\boldsymbol{p}'}^2+i0^+}\right]\Bigg\{[1-2f(\omega')]V_c(|\boldsymbol{p}-\boldsymbol{p}'|)$$
$$+\int_0^\infty\frac{d\Omega}{\pi}\mathrm{Im}\tilde{V}_{ee}^R(\boldsymbol{p}-\boldsymbol{p}',\Omega)\Bigg[[f(-\omega')+n(\Omega)]\left(\frac{1}{\omega+\Omega+\omega'+i0^+}-\frac{1}{\omega-\Omega-\omega'+i0^+}\right)$$
$$+[f(\omega')+n(\Omega)]\left(\frac{1}{\omega-\Omega+\omega'+i0^+}-\frac{1}{\omega+\Omega-\omega'+i0^+}\right)\Bigg]\Bigg\}$$

$$G_{\boldsymbol{p}}(i\omega_p)=-\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\mathrm{Im}G_{\boldsymbol{p}}^R(\omega')}{i\omega_p-\omega'}$$

$$\tilde{V}_{ee}(\boldsymbol{q},i\omega_q)=V_c(q)-\int_0^\infty\frac{d\Omega}{\pi}\frac{2\Omega}{(i\omega_q)^2-\Omega^2}\mathrm{Im}\tilde{V}_{ee}^R(\boldsymbol{q},\Omega)$$

BCS-like Gap Equation

Define
$$\Delta_{\boldsymbol{p}}\equiv 2|\xi_{\boldsymbol{p}}|\int_0^\infty\frac{d\omega}{\pi}\mathrm{Im}\left[\frac{\phi_{\boldsymbol{p}}^R(\omega)}{\omega^2-\xi_{\boldsymbol{p}}^2+i0^+}\right]$$

$$\Delta_{\boldsymbol{p}}=-\sum_{\boldsymbol{p}'}\frac{\Delta_{\boldsymbol{p}'}}{2|\xi_{\boldsymbol{p}'}|}\Bigg\{[1-2f(|\xi_{\boldsymbol{p}'}|)]\left[V_c(|\boldsymbol{p}-\boldsymbol{p}'|)+\int_0^\infty\frac{2}{\pi}d\Omega\frac{\mathrm{Im}\tilde{V}_{ee}^R(\boldsymbol{p}-\boldsymbol{p}',\Omega)}{\Omega+|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}\right]$$
$$+\int_0^\infty\frac{2}{\pi}d\Omega\,\mathrm{Im}\tilde{V}_{ee}^R(\boldsymbol{p}-\boldsymbol{p}',\Omega)[f(|\xi_{\boldsymbol{p}'}|)+n(\Omega)]$$
$$\times\left[\frac{1}{\Omega+|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}+\frac{\theta(|\xi_{\boldsymbol{p}'}|-\Omega)}{-\Omega+|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}+\frac{\theta(-|\xi_{\boldsymbol{p}'}|+\Omega)}{-\Omega-|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}\right]\Bigg\}$$

$$\Delta_{\boldsymbol{p}}=-\sum_{\boldsymbol{p}'}\frac{\Delta_{\boldsymbol{p}'}}{2\xi_{\boldsymbol{p}'}}\tanh\left(\frac{\xi_{\boldsymbol{p}'}}{2T_c}\right)\mathcal{K}_{\boldsymbol{p},\boldsymbol{p}'}$$

BCS-like gap equation obtained by integrating out ω-variables

$$\mathcal{K}_{\boldsymbol{p},\boldsymbol{p}'}\equiv V_c(|\boldsymbol{p}-\boldsymbol{p}'|)+\int_0^\infty\frac{2}{\pi}d\Omega\frac{\mathrm{Im}\tilde{V}_{ee}^R(\boldsymbol{p}-\boldsymbol{p}',\Omega)}{\Omega+|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}$$
$$=\int_0^\infty\frac{2}{\pi}d\Omega\frac{|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|}{\Omega^2+(|\xi_{\boldsymbol{p}}|+|\xi_{\boldsymbol{p}'}|)^2}\tilde{V}_{ee}(\boldsymbol{p}-\boldsymbol{p}',i\Omega)$$

The pairing interaction can be determined from first principles.

No assumption is made for pairing symmetry.

Summary for T_c from First Principles in G_0W_0

First-principles calculation of T_c without employing the concept of the Coulomb pseudopotential μ^*.

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 $T=T_c$

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

Pairing Interaction:

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

Here the smallness parameter is not ω_D/E_F, but the coupling constant.

◎ Derivation of this gap equation is given in: YT, JPSJ **45**, 786 (1978) , but I did not understand the real meaning of this pairing interaction until late 2000's.

SCDFT

Extension of DFT to treat superconductivity (SCDFT)

→ Basic variables: $n(\boldsymbol{r})$ and $\chi(\boldsymbol{r},\boldsymbol{r}')$

cf. Oliveira, Gross & Kohn, PRL**60**, 2430 (1988).

- Electron Pair Density: $\chi(\mathbf{r},\mathbf{r}')(\equiv\langle\Psi_\uparrow(\mathbf{r})\Psi_\downarrow(\mathbf{r}')\rangle)$
- Exchange-Correlation Energy Functional: $F_{xc}[n(\mathbf{r}),\chi(\mathbf{r},\mathbf{r}')]$
- Exchange-Correlation Pair Potential: $\Delta_{xc}(\mathbf{r},\mathbf{r}')=-\delta F_{xc}[n,\chi]/\delta\chi^*(\mathbf{r},\mathbf{r}')$

$$\Delta_i = -\sum_j\frac{\Delta_j}{2\varepsilon_j}\tanh\frac{\varepsilon_j}{2T_c}\mathcal{K}_{ij}$$

ε_i : Kohn-Sham level

Δ_i : Gap function for KS orbital i

$\mathcal{K}_{ij}$: Pairing interaction (Second functional derivative of $F_{xc}[n,\chi]$ with respect to χ^* and χ)

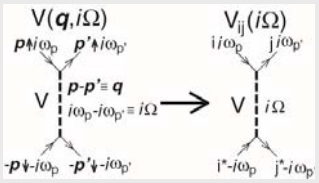
K_{ij} in the Weak-Coupling Region

Good correspondence!

$$\Delta(\mathbf{p}) = -\sum_{\mathbf{p}'} \frac{\Delta(\mathbf{p}')}{2\varepsilon_{\mathbf{p}'}} \tanh\frac{\varepsilon_{\mathbf{p}'}}{2T_c} V_{\mathbf{p},\mathbf{p}'} \quad \leftrightarrow \quad \Delta_i = -\sum_j \frac{\Delta_j}{2\varepsilon_j} \tanh\frac{\varepsilon_j}{2T_c} \mathcal{K}_{ij}$$

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

→ $$\mathcal{K}_{ij} = \int_0^\infty \frac{2}{\pi} d\Omega \frac{|\varepsilon_i| + |\varepsilon_j|}{\Omega^2 + (|\varepsilon_i| + |\varepsilon_j|)^2} V_{ij}(i\Omega)$$



i^*: time-reversed orbital of the KS orbital i

For the problem of determining T_c, the KS orbitals can be determined uniquely as a functional of the exact normal-state $n(r)$.

Scheme for determining T_c in *inhomogeneous* electron systems in the weak-coupling region

Merits of This Functional Form

From the side of the Green's function approach:

→ For normal properties, we recently come to know that G_0W_0 is much better than GW (← corresponding to the Eliashberg theory in superconductivity). As long as we do not know about a proper form of the vertex function and ω_D/E_F is not small enough, G_0W_0 should be adopted instead of GW, recommending to use this functional form for the pairing interaction for a wide range of applications.

From the side of SCDFT:

→ This functional is an analogue to LDA for calculating normal-state properties. Although it do not always provide accurate enough information, LDA still always gives useful information at least for the initial investigation of actual materials. The same would be true for first-principles calculation of T_c with this functional.

$SrTiO_3$: Old Results

◎ Ti 3d electrons (near the Γ point in the BZ) superconduct with the exchange of the soft ferroelectric phonon mode

cf. YT, JPSJ**49**, 1267 (1980)

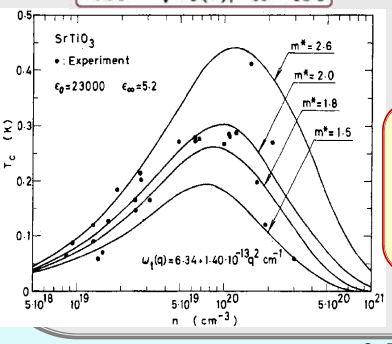
$$\tilde{V}_{ee}(\boldsymbol{q}, i\Omega) = \frac{4\pi e^2}{\varepsilon(\boldsymbol{q}, i\Omega) q^2}$$

$$\varepsilon(\boldsymbol{q}, i\Omega) = \varepsilon_\infty + \frac{4\pi e^2}{q^2}\Pi^0(\boldsymbol{q}, i\Omega) + [\varepsilon_0(\boldsymbol{q}) - \varepsilon_\infty]\frac{\omega_{qTO}^2}{\Omega^2 + \omega_{qTO}^2}$$

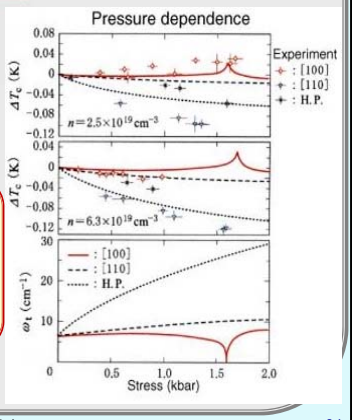
$$\varepsilon_0(\boldsymbol{q}) = \varepsilon_0(\boldsymbol{0})\omega_{\boldsymbol{0}TO}^2/\omega_{qTO}^2$$

$$\omega_{\boldsymbol{0}LO} = \sqrt{\varepsilon_0(\boldsymbol{0})/\varepsilon_\infty}\ \omega_{\boldsymbol{0}TO}$$

m^* (band-edge mass) is the only parameter in determining T_c.

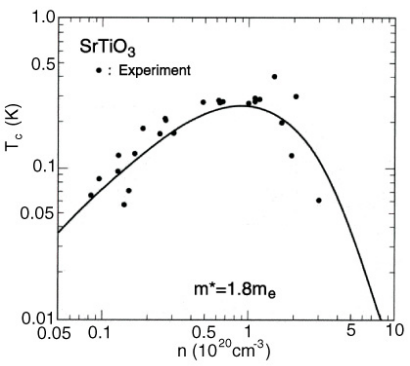


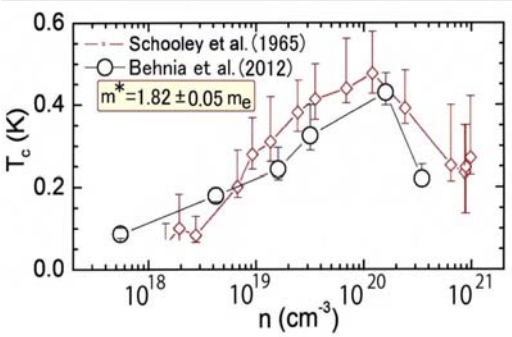
$m^*=1.8m_e$ is most probable. Pressure effects are investigated with this m^*.



$SrTiO_3$:Compare with New Experiment

Recent experimental result:
Lin, Zhu, Fauque, & Behnia, PRX**3**, 021002 (2013)



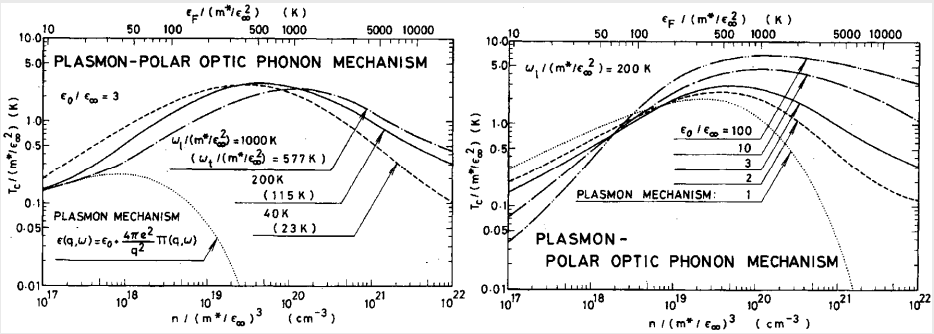


YT, JPSJ**49**, 1267 (1980)

Plasmon-Polar Phonon Combined Mechanism

Calculated T_c for the many-electron Fröhlich model

YT, JPSJ **49**, 1267 (1980)



- Optimum density exists with $T_c^{max} \sim (5\text{-}10)m^*/\varepsilon_\infty^2$ K.
- At very low densities, the polar phonons do not contribute; i.e., only the plasmons contribute to give $T_c/E_F \sim 0.04$.

Uemura Plot

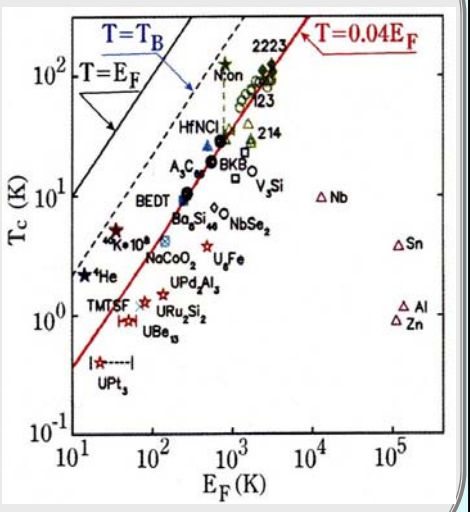
Uemura Plot:

Plot of T_c as a function of E_F obtained by the penetration depth

Y. J. Uemura et l., PRL**66**, 2665 (1991); Nature **352**, 605 (1991).

Will high-T_c be obtained under the condition of $\omega_D/E_F \ll 1$?
← Not at all!

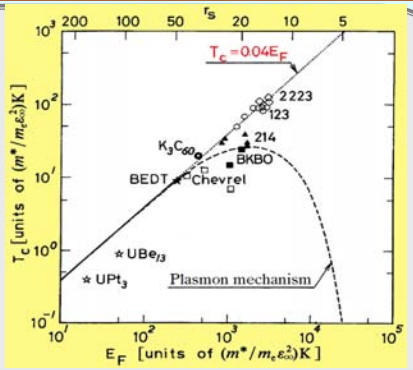
In the phonon mechanism, T_c/ω_D is known to be less than about 0.05. Because $T_c/E_F = (T_c/\omega_D)(\omega_D/E_F)$, this indicates that ω_D/E_F should be of the order of unity. Thus interesting high-T_c materials cannot be studied by the conventional Eliashberg theory!!



Plasmon as Universal Mechanism

The universal value $T_c/E_F \sim 0.04$ is reproduced in the plasmon mechanism!

YT, JPSJ**61**, 3849 (1992).



Why is this the case?

→ All the metallic low-carrier density systems are described by the Hamiltonian of the electron gas, as long as $p_F^{-1} \ll a_0$.

$$H=\sum_{\mathbf{p}\sigma}\varepsilon_{\mathbf{p}}c^\dagger_{\mathbf{p}\sigma}c_{\mathbf{p}\sigma}+\sum_{\mathbf{p}\sigma}\sum_{\mathbf{K}\neq 0}S_a(\mathbf{K})V_{ps}(\mathbf{p},\mathbf{p}+\mathbf{K})c^\dagger_{\mathbf{p}\sigma}c_{\mathbf{p}+\mathbf{K}\sigma}$$
$$+\frac{1}{2}\sum_{\mathbf{q}\neq 0}\sum_{\mathbf{p}\sigma}\sum_{\mathbf{p}'\sigma'}\frac{4\pi e^2}{\mathbf{q}^2}c^\dagger_{\mathbf{p}+\mathbf{q}\sigma}c^\dagger_{\mathbf{p}'-\mathbf{q}\sigma'}c_{\mathbf{p}'\sigma'}c_{\mathbf{p}\sigma}$$

$$\varepsilon_{\mathbf{p}}=\frac{\mathbf{p}^2}{2m}+V_{ps}(\mathbf{p},\mathbf{p}),\quad \text{Atomic structure factor: } S_a(\mathbf{q})$$

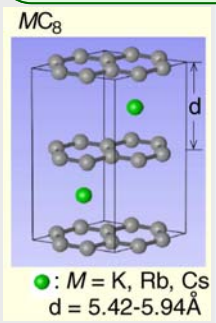
$$S_a(\mathbf{q})=\left(\frac{1}{n_i}\sum_{j_0}e^{i\mathbf{q}\cdot\mathbf{d}_{j_0}}\right)\frac{1}{N_a}\sum_{j_1j_2j_3}e^{ij_1\mathbf{q}\cdot\mathbf{a}_1}e^{ij_2\mathbf{q}\cdot\mathbf{a}_2}e^{ij_3\mathbf{q}\cdot\mathbf{a}_3}$$

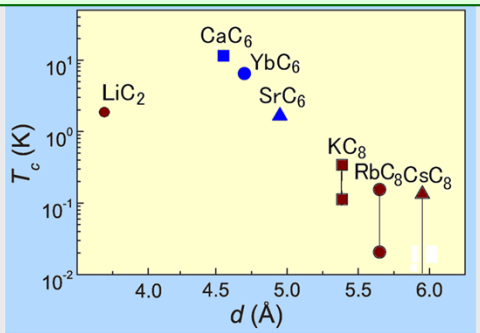
More on Superconductivity in the Electron Gas

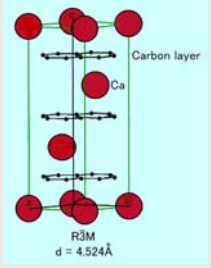
1) Kohn-Luttinger, PRL **15**, 524 (1965): Stress on Friedel oscillation; $l > 0$; T_c<<1K
2) YT, JPSJ **45**, 786 (1978): G_0W_0 approximation; $T_c \sim$ 1-10K at low densities
3) Rietschel-Sham, PRB **28**, 5100 (1983): GW_0approximation; $T_c \sim$100K
4) Grabowski-Sham, PRB **29**, 6132 (1984): Inclusion of 1st-order vertex; no SC
5) Shirron-Ruvalds, PRB **34**, 7596 (1986): With static local-field correction
6) YT, PRB **37**, 155 (1988): Variational approach with correlated BCS function; Inclusion of more than 40 vertex corrections; Similar results with that in G_0W_0
7) Kuechenhoff-Woelfle, PRB **38**, 935 (1988): Obtain the effective interaction by solving the Bethe-Salpeter equation; Extension of the approach in 1).
8) Canright-Vignale, PRB **39**, 2740 (1989): 2D version of 5).
9) YT, PRB **47**, 5202 (1993): Same approach as in 5), but extended to much lower densities to obtain the similar result as that in G_0W_0.
10) Richardson-Ashcroft, PRL **78**, 118 (1997); PRB **55**, 15130 (1997): Same approach as that in 5); Improvement on the local-field correction and simultaneously including the phonon effects to apply to the metallic hydrogen.
11) Gross group; PRL **100**, 257001 (2008); PRB **81,** 134505 & 134506 (2010): SCDFT applied to metallic hydrogen with T_c over 200K.
12) Akashi & Arita, PRL**111**, 057006 (2013); Verification of plasmon effect in actual systems: Li & Ca, and also recently in Li doped ZrNCl & HfNCl.

Graphite Intercalation Compounds

KC_8: T_c = 0.14K [Hannay *et al.*, *PRL**14***, 225(1965)]
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)]







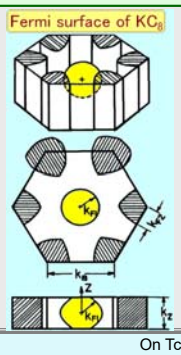
CaC_6

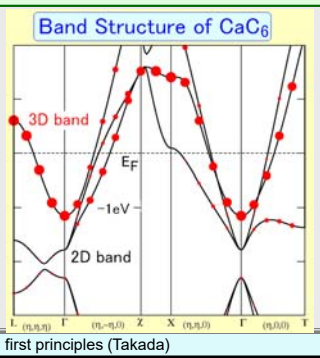
We should know the reason why T_c is enhanced by a hundred times by just changing K with Ca?

Electronic Structure

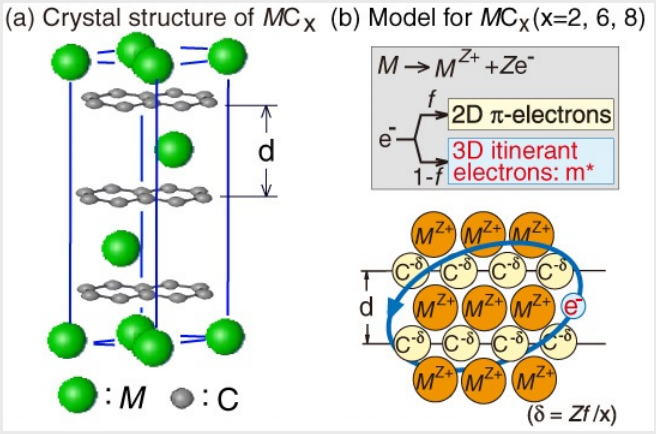
Band-structure calculation:
KC_8: [Ohno *et al.*, *JPSJ**47***, 1125(1979); Wang *et al.*, *PRB**44***, 8294(1991)]
LiC_2: [Csanyi *et al.*, *Nature Phys.**1***, 42 (2005)]
CaC_6, YbC_6: [Mazin,*PRL**95***,227001(2005);Calandra & Mauri,*PRL**95***,237002(2005)]

Important common features
(1) 2D- and 3D-electron systems coexist.
(2) Only 3D electrons (considered as a 3D homogeneous electron gas with the band mass m^*) in the interlayer state superconduct.





Microscopic Model for GICs



This model was proposed in 1982 for explaining superconductivity in KC_8: YT, JPSJ ***51***, 63 (1982) In 2009, it was found that the same model also worked very well for CaC_6: YT, JPSJ **78**, 013703 (2009).

Model Hamiltonian

First-principles Hamiltonian for polar-coupling layered crystals

cf. YT, *J. Phys. Soc. Jpn.* ***51***, 63 (1982)

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

$$H_{\mathrm{el-el}}=\frac{1}{2}\sum_{\boldsymbol{P}\boldsymbol{P}'}\sum_{\boldsymbol{Q}}\sum_{\sigma\sigma'}V^0(\boldsymbol{q},q_z)c^{+}_{\boldsymbol{P}+\boldsymbol{Q}\sigma}c^{+}_{\boldsymbol{P}'-\boldsymbol{Q}\sigma'}c_{\boldsymbol{P}'\sigma'}c_{\boldsymbol{P}\sigma}$$

$$+\sum_{\boldsymbol{p}\boldsymbol{p}'}\sum_{\boldsymbol{q}}\sum_{iv}\sum_{\sigma\sigma'}\sum_{j}{\sum_{k_z}}'V^0\left(\boldsymbol{q},k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)\mathrm{e}^{ik_zz_i}a^{+}_{iv\boldsymbol{p}+\boldsymbol{q}\sigma}c^{+}_{\boldsymbol{p}'-\boldsymbol{q},p_z'-k_z-(2\pi/d)j\sigma'}c_{\boldsymbol{p}'p_z'\sigma'}a_{iv\boldsymbol{p}\sigma}$$

$$+\frac{1}{2}\sum_{\boldsymbol{p}\boldsymbol{p}'}\sum_{\boldsymbol{q}}\sum_{ii'}\sum_{vv'}\sum_{\sigma\sigma'}\sum_{j}{\sum_{k_z}}'V^0\left(\boldsymbol{q},k_z+\frac{2\pi}{d}j\right)F\left(k_z+\frac{2\pi}{d}j\right)^2\exp\{ik_z(z_i-z_{i'})\}\,a^{+}_{iv\boldsymbol{p}+\boldsymbol{q}\sigma}a^{+}_{i'v'\boldsymbol{p}'-\boldsymbol{q}\sigma'}a_{i'v'\boldsymbol{p}'\sigma'}a_{iv\boldsymbol{p}\sigma}$$

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

$$+\sum_{i\lambda}\sum_{\sigma}\sum_{\boldsymbol{p}\boldsymbol{k}}{\sum_{k_z}}'g_{i\lambda}(\boldsymbol{k})a^{+}_{iv\boldsymbol{p}+\boldsymbol{k}\sigma}a_{iv\boldsymbol{p}\sigma}b_{\lambda\boldsymbol{k}}+\mathrm{c.c.}$$

with

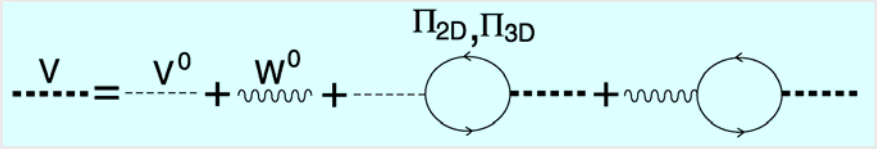
$$g_{\lambda}\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)=i\sqrt{V^0\left(\boldsymbol{k},k_z+\frac{2\pi}{d}j\right)\Big/2\omega_{\lambda}(\boldsymbol{K})}\;G_{j\lambda}(\boldsymbol{K})$$

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

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

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

Effective Electron-Electron Interaction in RPA



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

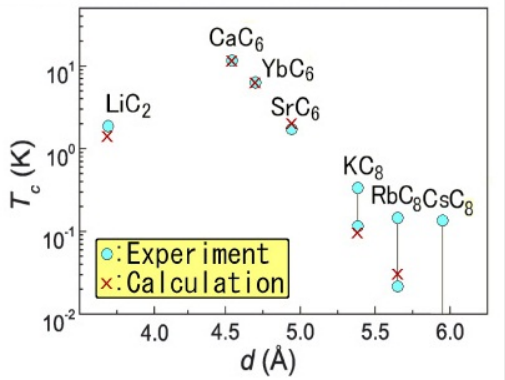
$$V^0(q, q_z) = 4\pi e^2 / (\varepsilon_\infty^{\perp} q^2 + \varepsilon_\infty^{//} q_z^2), \quad E_j(K, \omega) = 1 + \sum_{\lambda} \frac{G_{j\lambda}(K)^2}{\omega^2 - \omega_\lambda(K)^2}, \quad (\lambda = \text{TA or TO})$$

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

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

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

Calculated Results for T_c

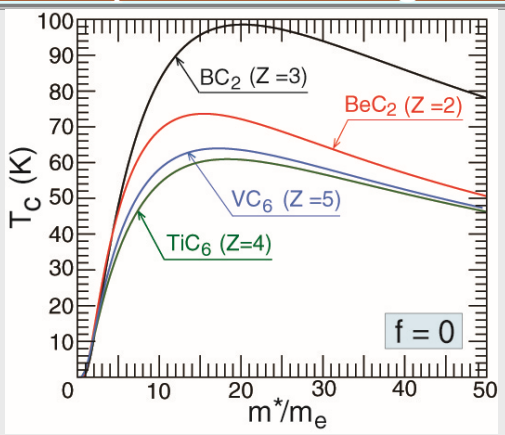


YT, JPSJ **78**, 013703 (2009).

		K	Ca
Valence	Z	1	2
Layer separation	d	~ 5.5A	~ 4.5A
Branching ratio	f	~ 0.6	~ 0.15
Band mass	m^*	~ m_e (s-like)	~ $3m_e$ (d-like)

cf. Atomic mass m_M is about the same.

Perspectives for Higher T_c



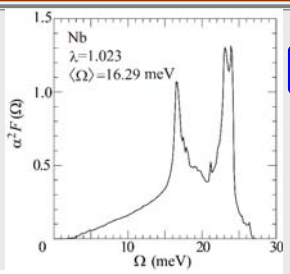
YT, JPSJ **78**, 013703 (2009).

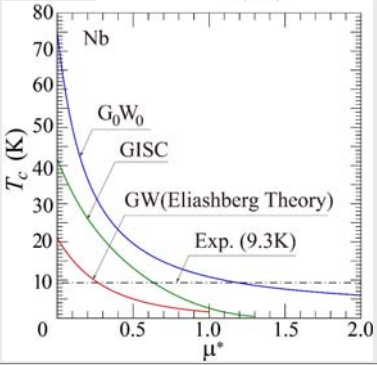
◎ Two key controlling parameters: Z and m^*.

◎ T_c will be raised by a few times from the current value of 15K, but never go beyond100K.

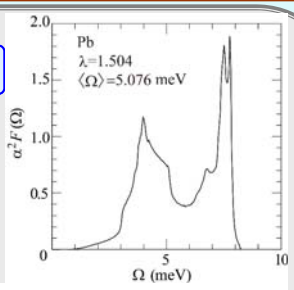
強結合電子フォノン系の場合

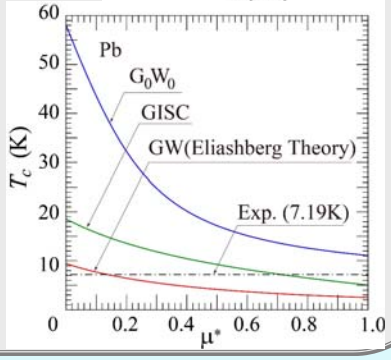
λ=1.023





λ=1.504

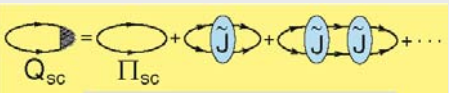




Dynamical Pair Correlation Function

$Q_{sc}(\boldsymbol{q},\omega)$; $Q_{sc}(\boldsymbol{q}=\boldsymbol{0},\omega\to 0)$ at $T=T_c$

Green's-Function approach:

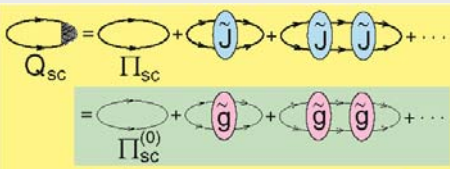


Q_{sc} : Pairing Correlation Function

Π_{sc} : Pairing Polarization Function

$\tilde{J}$: Irreducible Electron-Electron Effective Interaction

DFT approach:



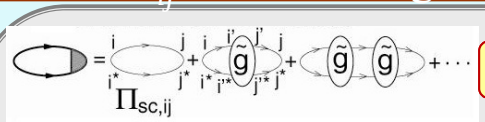
$\Pi_{sc}^{(0)}$: Pairing Polarization Function in the noninteracting system

$\tilde{g} \equiv \tilde{J} + \Pi_{sc}^{-1} - \Pi_{sc}^{(0)-1}$

$$Q_{sc} = -\frac{\Pi_{sc}}{1+\tilde{J}\,\Pi_{sc}} \rightarrow Q_{sc} = -\frac{\Pi_{sc}^{(0)}}{1+\tilde{g}\,\Pi_{sc}^{(0)}}$$

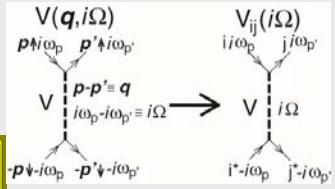
In this definition of $\tilde{g}$, *both vertex and self-energy corrections are simultaneously included, in good corresponding to the Ward identity.*

K_{ij} in the Strong-Coupling Region



Q_{sc} in terms of KS orbitals

$$\Delta_i = -\sum_j \frac{\Delta_j}{2\varepsilon_j} \tanh\frac{\varepsilon_j}{2T_c} \mathcal{K}_{ij}$$

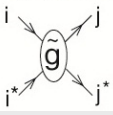


Weak-coupling case

$$\mathcal{K}_{ij} = \int_0^\infty \frac{2}{\pi} d\Omega \frac{|\varepsilon_i| + |\varepsilon_j|}{\Omega^2 + (|\varepsilon_i| + |\varepsilon_j|)^2} V_{ij}(i\Omega)$$

Use $\tilde{g}_{ij}$ instead of V_{ij} in the general case!

$\tilde{g}_{ij}$ in terms of KS orbitals



In the strong-coupling region, the Ω-dependence of $\tilde{g}$ will be weak.

Note: $\tilde{g}$ corresponds to f_{xc} in TDDFT!

TDDFT $f_{xc} = \Pi^{-1} - \Pi^{(0)-1}$

ξ_0 in the BCS Theory

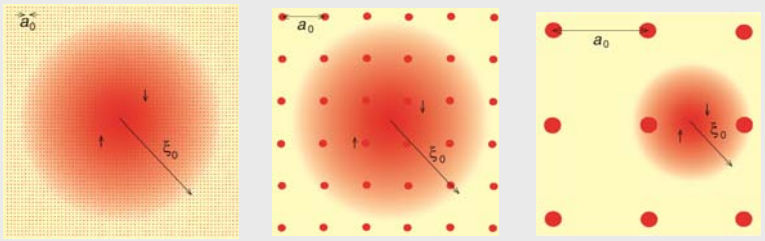
$$\xi_0 = \frac{v_F}{\pi \Delta_0}, \quad \frac{2\Delta_0}{T_c} = 3.53 \quad \Big\} \quad \frac{T_c}{E_F} = \frac{0.361}{p_F \xi_0}$$

$T_c = 10^{-4}$–$10^{-3}\, E_F \longrightarrow \xi_0 = 100$-$1000$ nm

$T_c \approx 0.04 E_F \longrightarrow \xi_0 \approx 2a_0$

a_0: lattice constant

High-T_c → Inevitably associated with short ξ_0



Formulate a scheme to calculate the pairing interaction from the zero-ξ_0 limit in real-space approach.

Evaluation of the Pairing Interaction

$$Q_{sc} = -\frac{\Pi_{sc}^{(0)}}{1 + \tilde{g}\,\Pi_{sc}^{(0)}}$$

N-site system

(1) Calculate $Q_{sc}^{(N)}$ by exact diagonalization

(2) Obtain $\tilde{g}_N$ by $\tilde{g}_N = -Q_{sc}^{(N)\,-1} - \Pi_{sc}^{(0:N)\,-1}$

$$Q_{sc}^{(N)} = -\frac{\Pi_{sc}^{(0:N)}}{1 + \tilde{g}_N \Pi_{sc}^{(0:N)}}$$

(3) Evaluate $\tilde{g}$ by $\lim_{N\to\infty} \tilde{g}_N$ Take $\tilde{g} = \tilde{g}_N$.

Basic observation: The essential physics of electron pairing can be captured in an N-site system, if the system size is large enough in comparison with ξ_0.
→ If ξ_0 is short, N may be taken to be very small.

Fullerene Superconductors

◎ Alkali-doped fullerene superconductors

1) Molecular crystal composed of C_{60} molecules
2) Superconductivity appears with T_c =18-38K in the half-filled threefold narrow conduction bands (bandwidth W~0.5eV) derived from the t_{1u}-levels in each C_{60} molecule.
3) The phonon mechanism with high-energy (ω_0~ 0.2eV) intramolecular phonons is believed to be the case, although the intramolecular Coulomb repulsion U is also strong and is about the same strength as the phonon-mediated attraction $-2\alpha\omega_0$ with α the electron-phonon coupling strength (α~ 2).
→ $U \approx 2\alpha\omega_0$

cf. O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

Hubbard-Holstein Model

Band-multiplicity:

It may be important in discussing the absence of Mott insulating phase [Han, Koch, & Gunnarsson, PRL**84**, 1276 (2000)], but it is not the case for discussing superconductivity [Cappelluti, Paci, Grimaldi, & Pietronero, PRB**72**, 054521 (2005)].

The simplest possible model to describe this situation is:

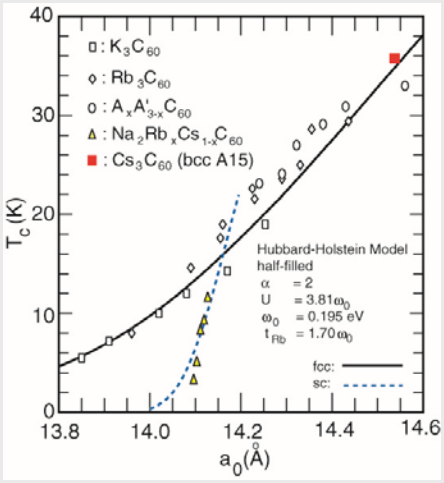
Hubbard-Holstein Model

$$H = -t \sum_{<i,j>,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_i H_i$$

$$H_i = -\mu \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} + U c^{\dagger}_{i\uparrow} c_{i\uparrow} c^{\dagger}_{i\downarrow} c_{i\downarrow} + \omega_0 a^{\dagger}_i a_i + \sqrt{\alpha}\omega_0 \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} (a_i + a^{\dagger}_i)$$

Assume $\tilde{g} = \tilde{g}_2$: 2-site calculation, because ξ_0 is very short (less than $2a_0$) . *cf.* YT, JPSJ**65**, 1544, 3134 (1996).

Electron-Doped C_{60}



According to the band-structure calculation:

$$t = t_{\mathrm{Rb}} \frac{d}{d_{\mathrm{Rb}}} \exp\left(-\frac{d - d_{\mathrm{Rb}}}{\Delta}\right)$$

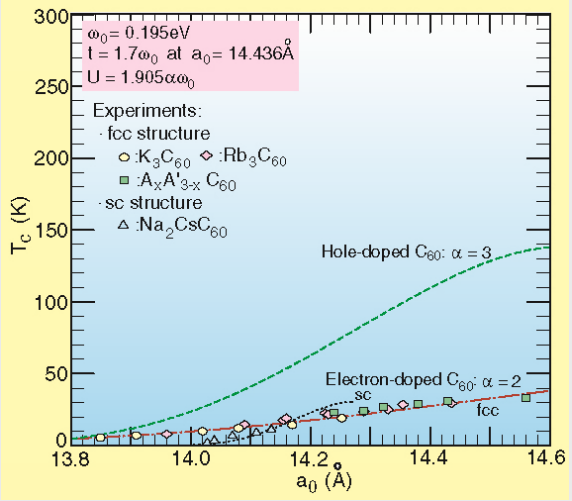
$$d = a_0/\sqrt{2} - 6.95\text{Å},\ \Delta = 0.55\text{Å}$$

The conventional electron-phonon parameter λ is about 0.6 for α=2.

The difference in T_c induced by that of the crystal structure including Cs_3C_{60} under pressure [Takabayashi *et al.*, Science **323**, 1589 (2009)] is successfully incorporated by that in $\Pi_{sc}^{(0)}$.

Hypothetical Hole-Doped C_{60}

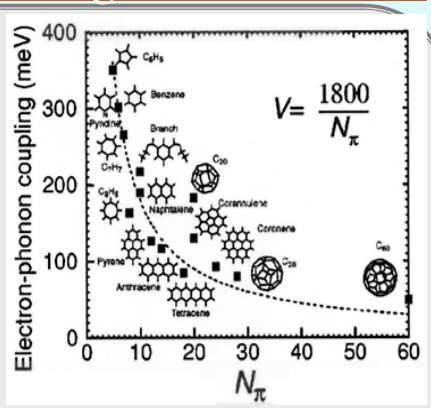
Hole-doped C_{60} : Carriers will be in the fivefold h_u valence band. → α =3



Case of Even Larger α

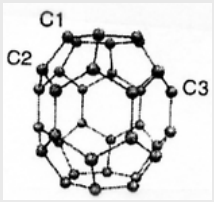
What happens for T_c, if α becomes even larger than 3?

A larger α is expected in a system with a smaller number of π-electrons N_π: A. Devos & M Lannoo, PRB**58**, 8236 (1998).



Case of C_{36} is interesting: α=4

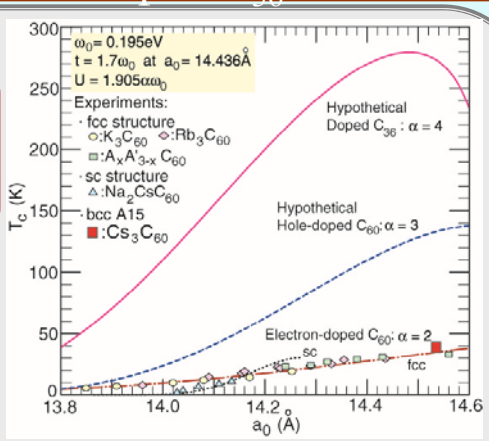
The C_{36} solid has already been synthesized: C. Piskoti, J. Yarger & A. Zettl, Nature **393**, 771 (1998); M. Cote, J.C. Grossman, M. L. Cohen, & S. G. Louie, PRL**81**, 697 (1998).



Hypothetical Doped C_{36}

If solid C_{36} is successfully doped → system with α =4

→ Room-temperature superconductor!



cf. For aromatic materials, the bond-phonon model like the Su-Schrieffer-Heeger one seems to be more realistic; the case of K_3 picene was studied in M. Casula et al., PRL**107**, 117006 (2011); PRB**86**, 075445 (2012).

Summary

1^0 In the weak-coupling region, the scheme in G_0W_0 provides more accurate results than the conventional Eliashberg scheme. In particular, the former determines the Coulomb pseudopotential μ^* from first principles.

2^0 A scheme based on SCDFT also provides T_c with similar accuracy for the phonon mechanism without the empirical parameter μ^*, but its current functional form for the pairing interaction is not good enough to treat the phonon mechanism and the electronic mechanisms on the same footing, contrary to the G_0W_0 scheme.

3^0 In the strong coupling and/or correlation region, much more work is needed in constructing the scheme for T_c from first principles.