

The mechanism of superconducting pairing in doped SrTiO_3
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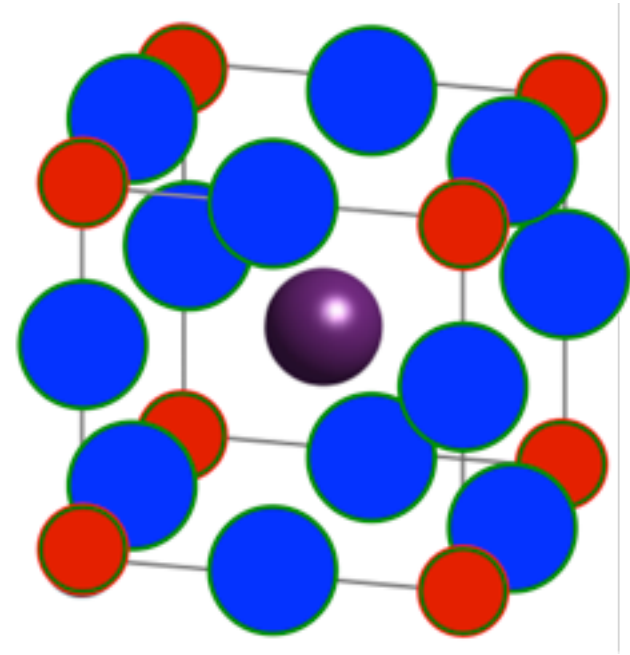


Francesco Barantani



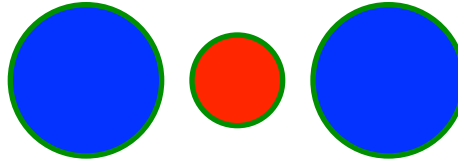
Enrico Giannini

SrTiO_3 : Ferro-electricity (requires ^{18}O)



$$T > T_c$$

Para Electric state



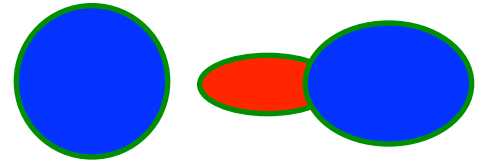
O^{2-}

Ti^{4+}

O^{2-}

$$T < T_c$$

Ferro Electric state



O^{2-}

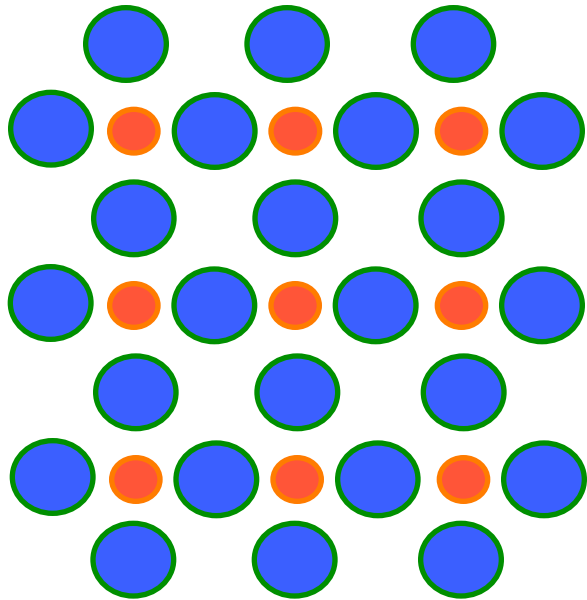
Ti^{4+}

O^{2-}

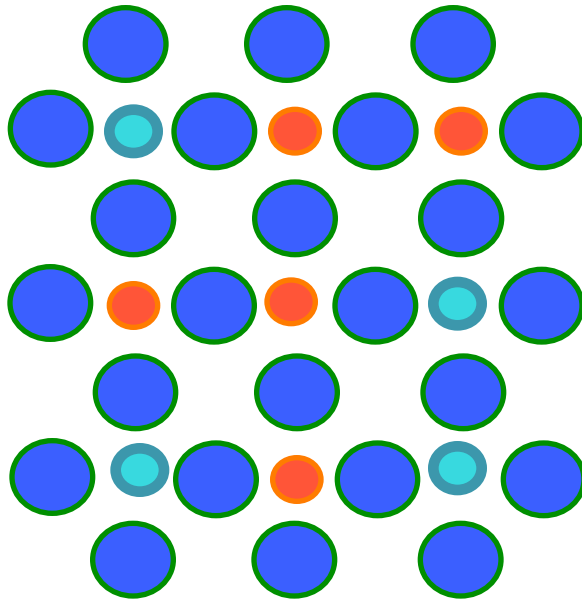
SrTiO₃: Superconductivity



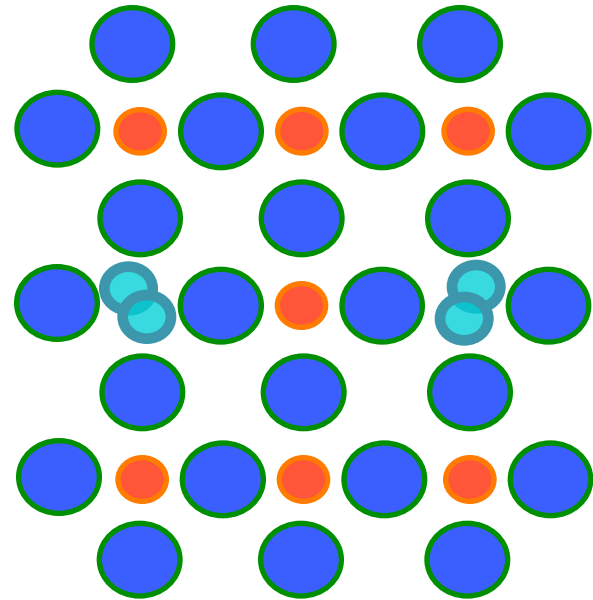
Undoped SrTiO₃
Insulator



Electron Doped
 $T > T_c$: Fermi Liquid



Electron Doped
 $T < T_c$: Cooper-Pairs



SrTiO₃: Ferroelectricity & Superconductivity

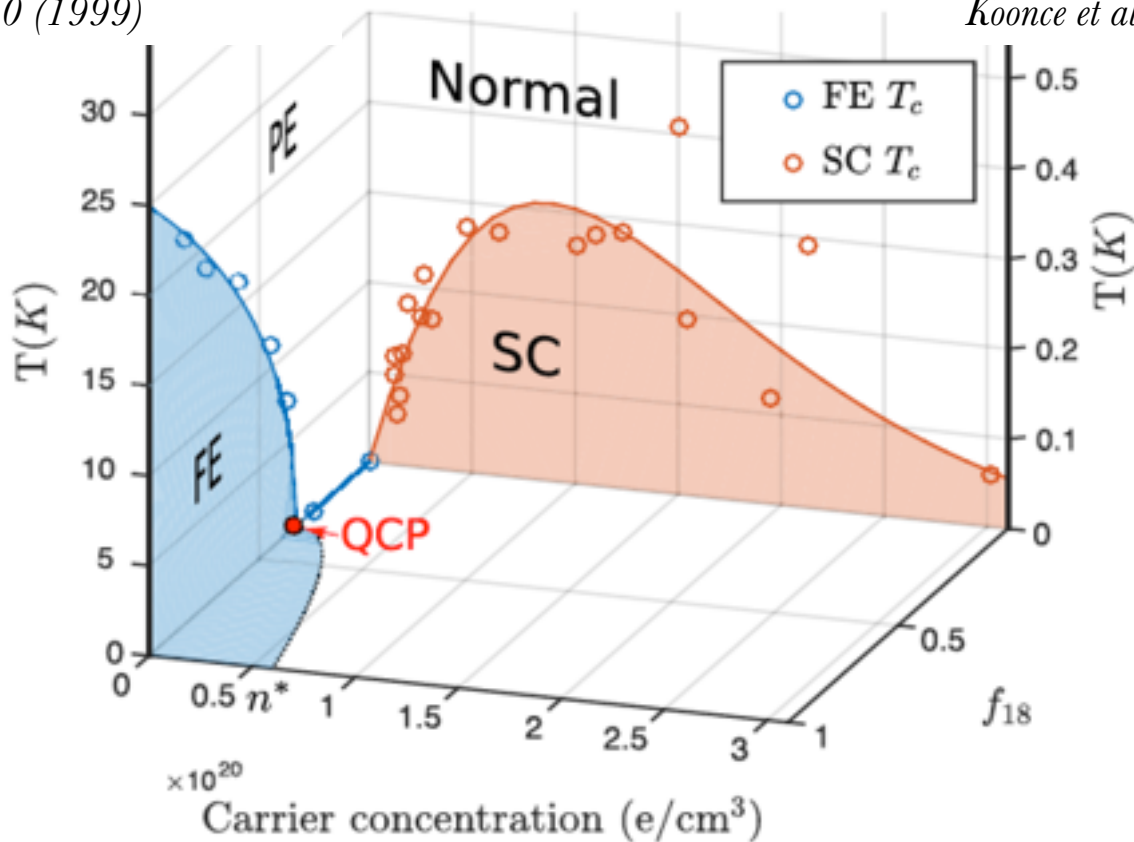


Müller & Burkhard, *PRB* 19, 3593 (1979)

Itoh et al, *PRL* 82, 3540 (1999)

Schooley et al, *PRL* 12, 474 (1964)

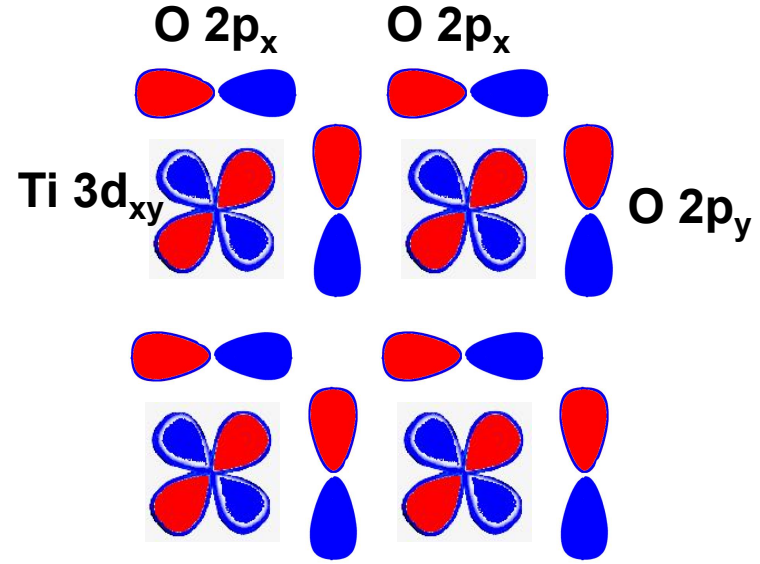
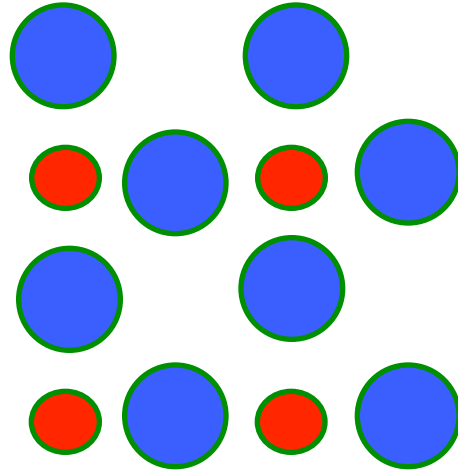
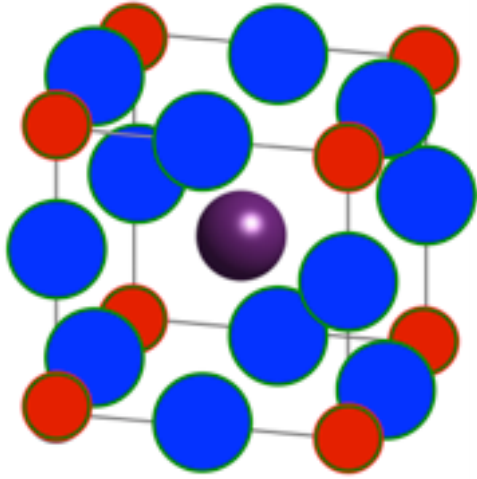
Koonce et al, *PR* 163, 380 (1967)



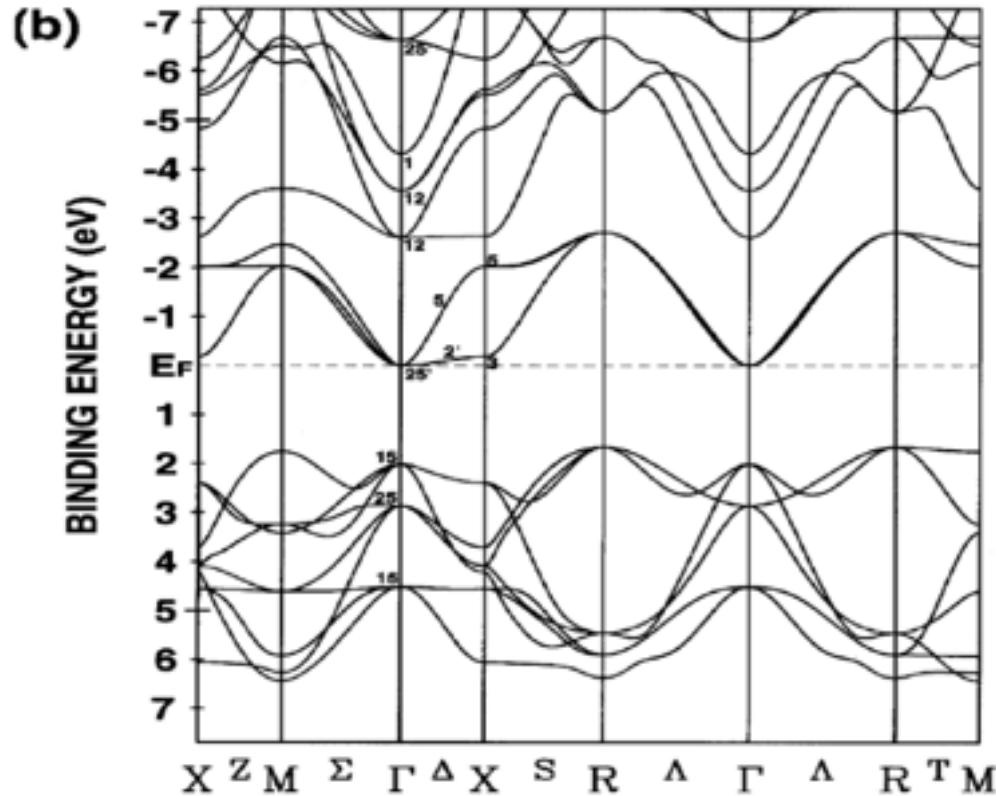
Rowley et al, *Nature Phys.* 10, 367 (2014)

JM Edge et al, *PRL* 115, 247002 (2015)

SrTiO₃: Crystal- and Band Structure



SrTiO₃ Band Structure

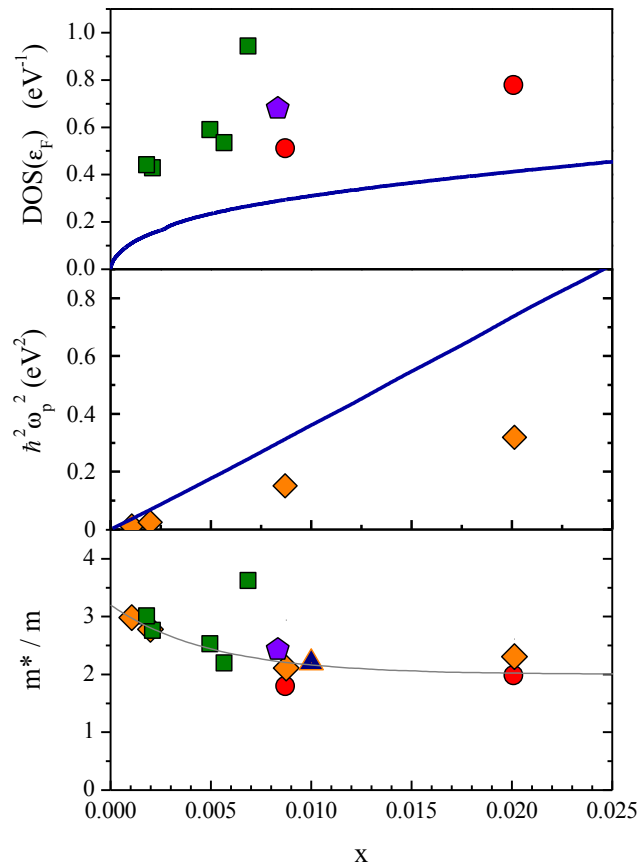


} Ti 3d(e_g) {x²-y², z²}

} Ti 3d(t_{2g}) {xy, yz, zx}

} O 2p

Electron doped SrTiO₃: Free Carrier Mass Enhancement



Specific Heat:

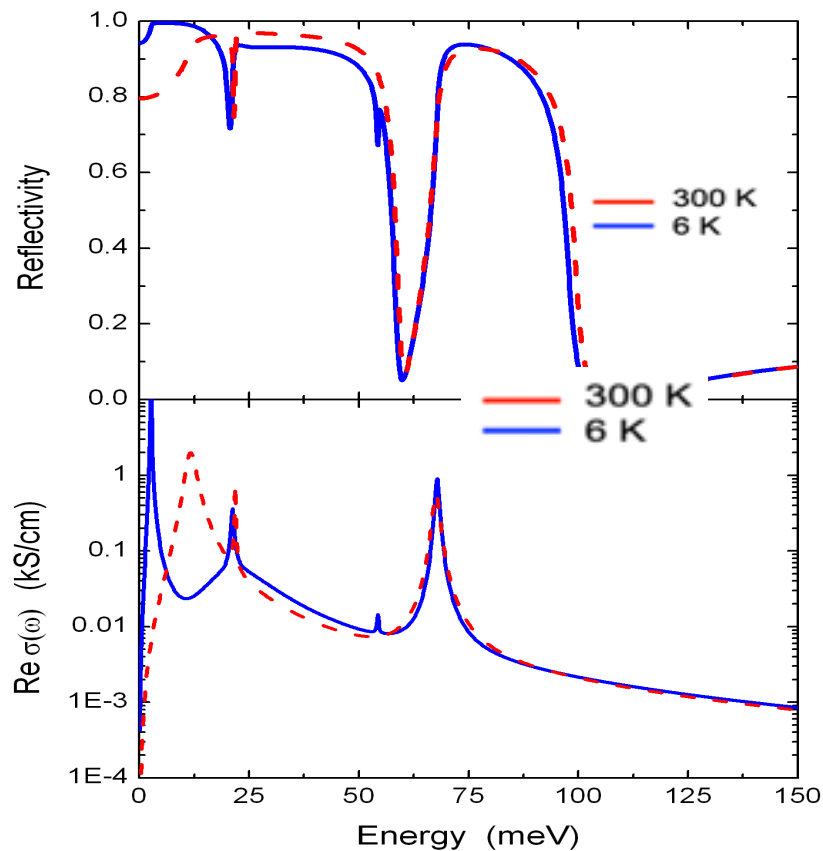
$$\frac{DOS_{SDH}}{DOS_{LDA}} = \frac{m^*}{m_{LDA}}$$

Free Carrier Spectral Weight:

$$\frac{\omega_{p,LDA}^2}{\omega_{p,exp}^2} = \frac{m^*}{m_{LDA}}$$

Free Carrier Mass Enhancement: $m^*/m \sim 2$

Electron coupling to longitudinal phonons



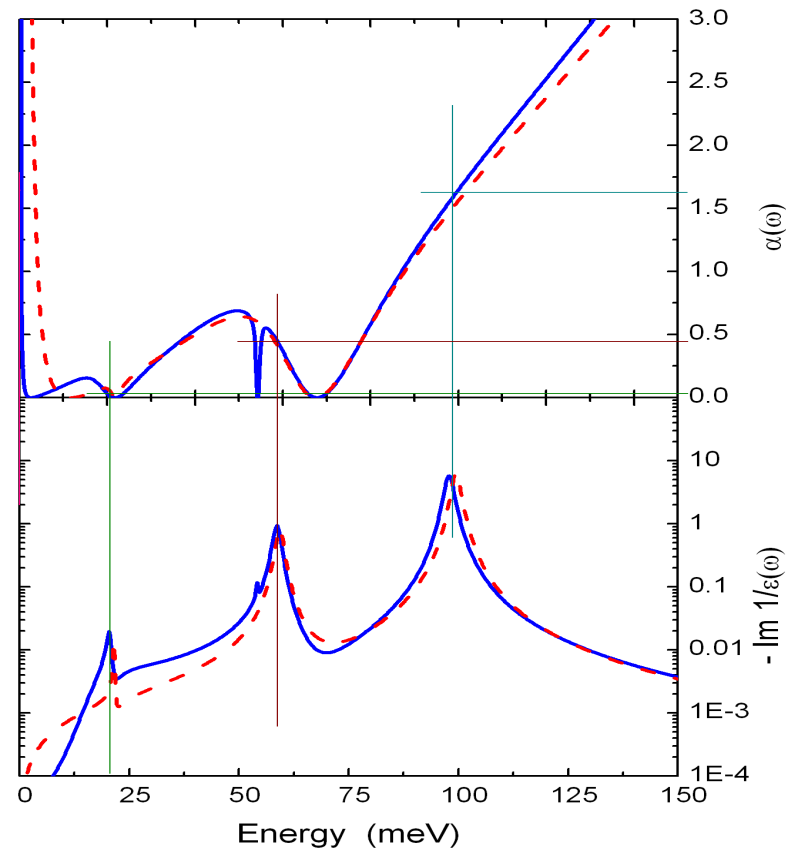
Electron coupling to longitudinal phonons



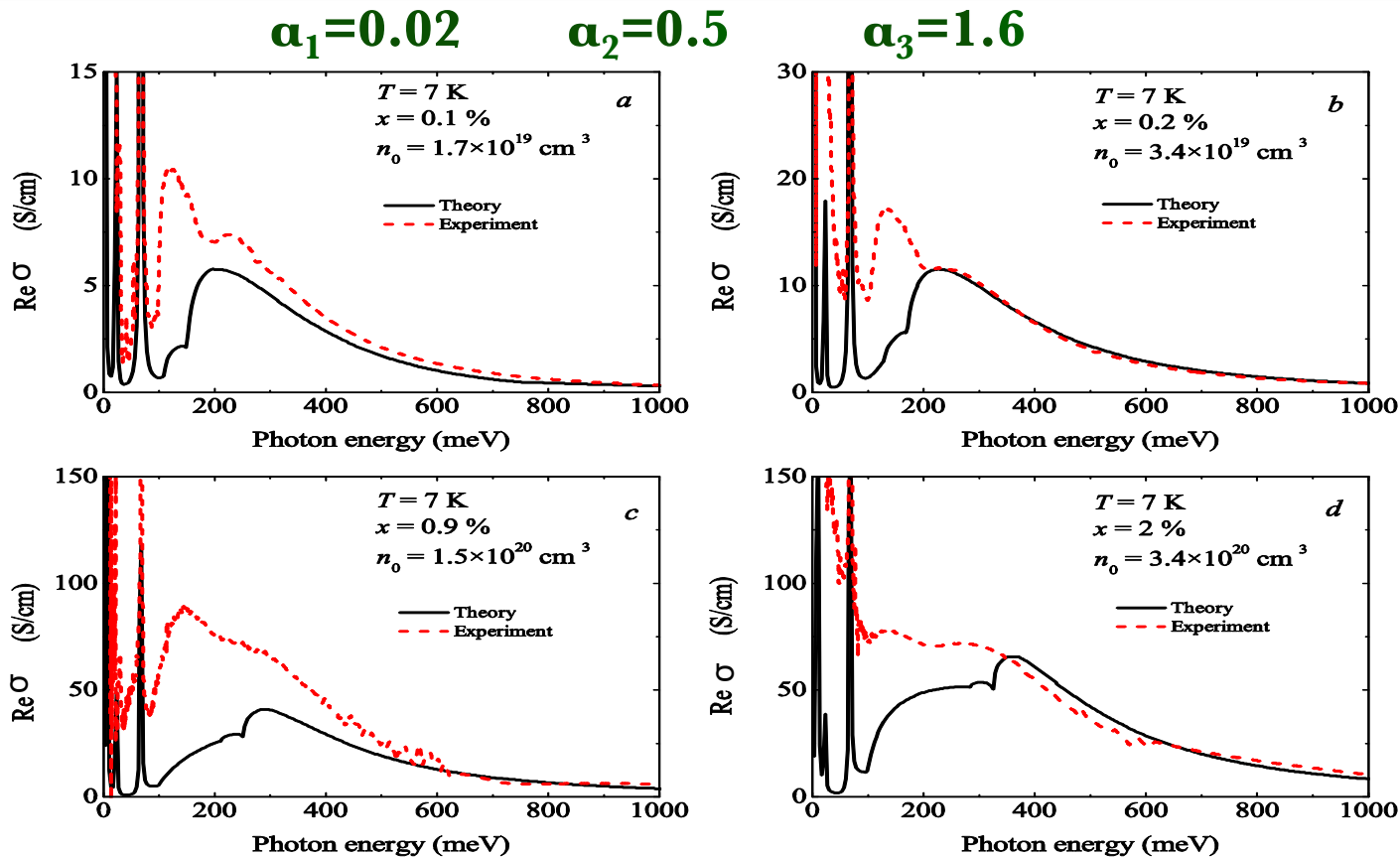
$$\alpha_j = \sqrt{\frac{2m_b}{\hbar^3 \omega_{L,j}^3}} \frac{q_e^2}{\left[\partial \epsilon / \partial \omega \right]_{L,j}}$$

Y. Toyozawa, in "Polarons in ionic crystals...", North Holland (1972)

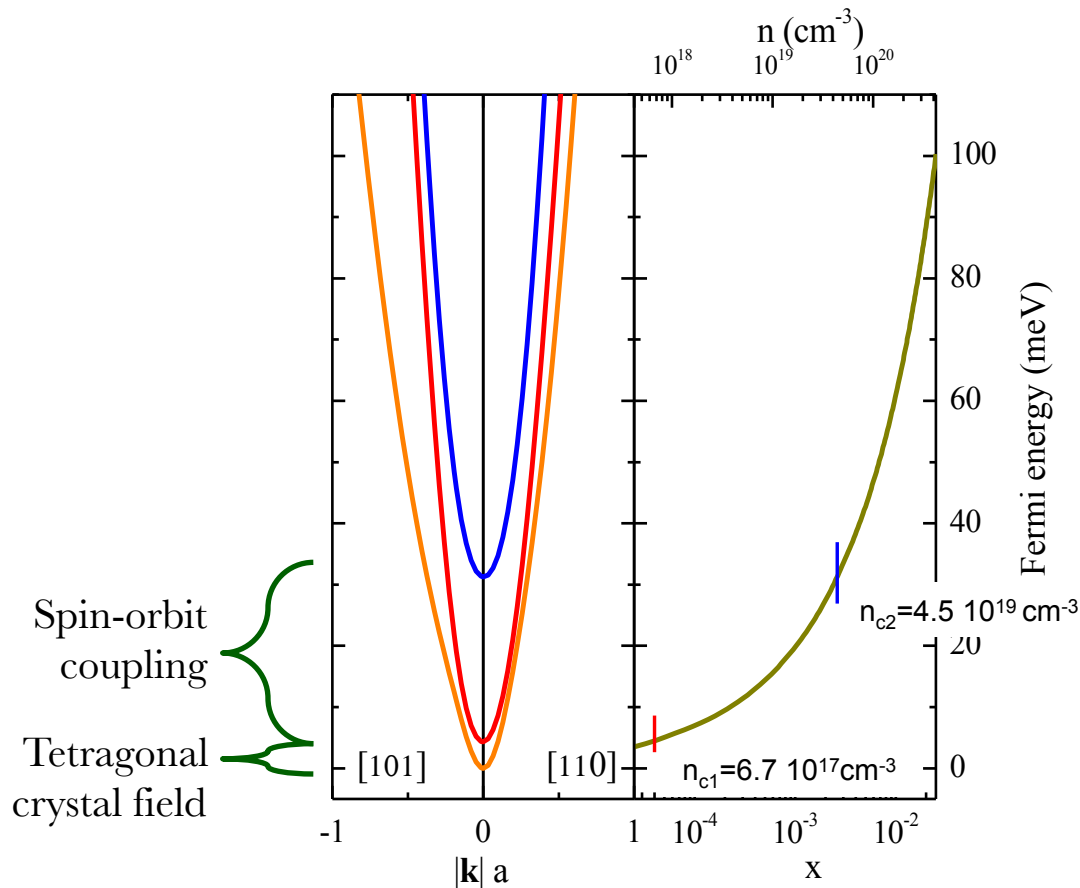
— 300 K
— 6 K



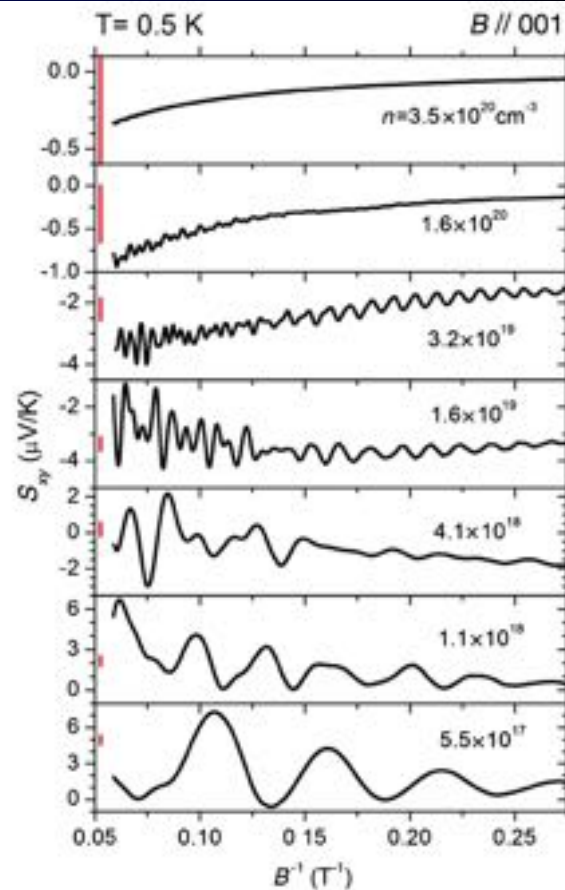
Electron coupling to longitudinal phonons



Electron Doped SrTiO₃ Band Structure



DvdM et al, PRB 84, 205111 (2011)



Lin et al, PRX 3, 021002 (2013)

Electron Doped SrTiO₃ Band Structure



The doped electrons in STO form large polarons ($m^*/m \sim 2.5$) due to EPI

These polarons form bands

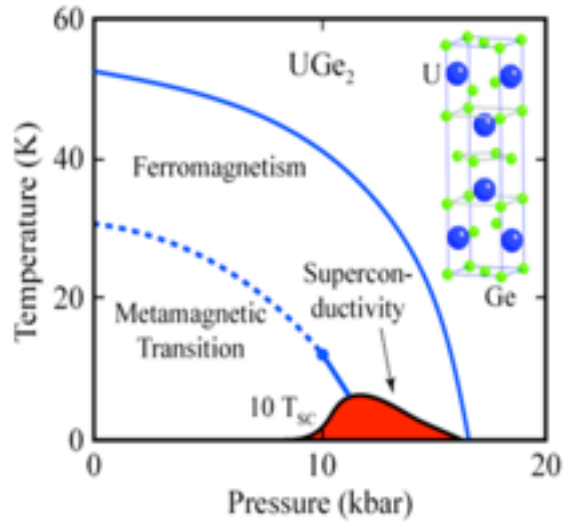
These bands satisfy the Luttinger theorem

The polaron liquid in doped SrTiO₃ is in this respect a normal Fermi liquid

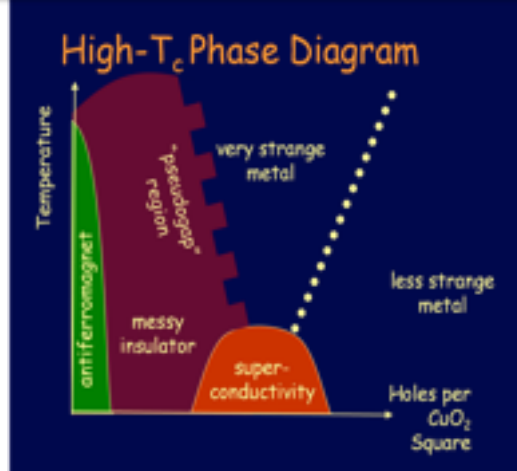
Snags vis à vis the adiabaticity condition, e.g. Migdal-Eliashberg



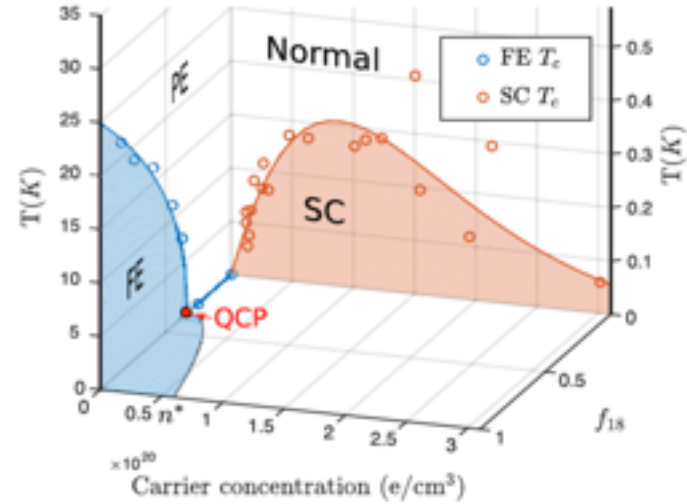
Quantum Criticality and Superconductivity



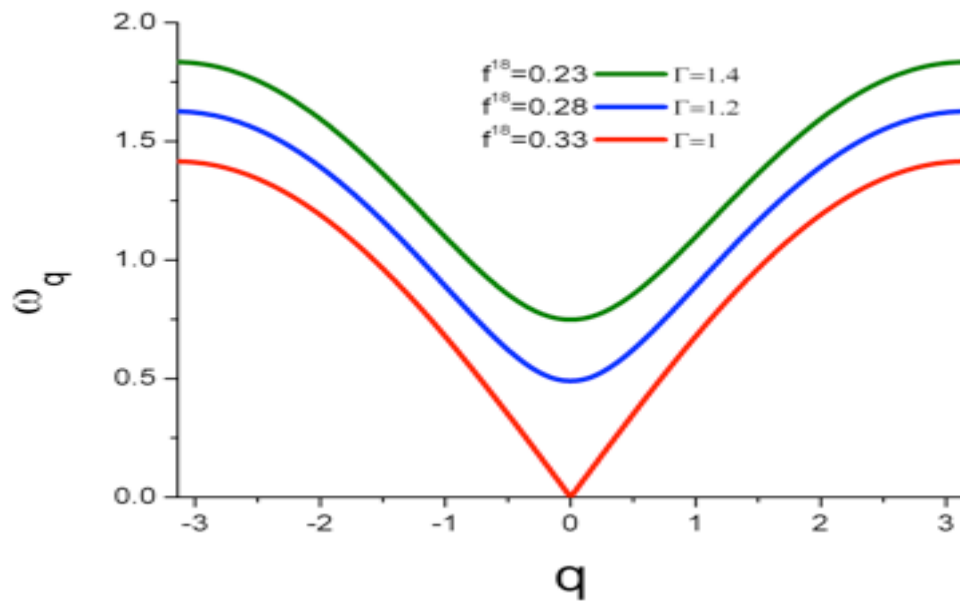
*S. S. Saxena et al,
Nature 406, 587 (2000)*



*J. L. Tallon, and J. W. Loram,
Physica C 349, 53-68 (2001)*

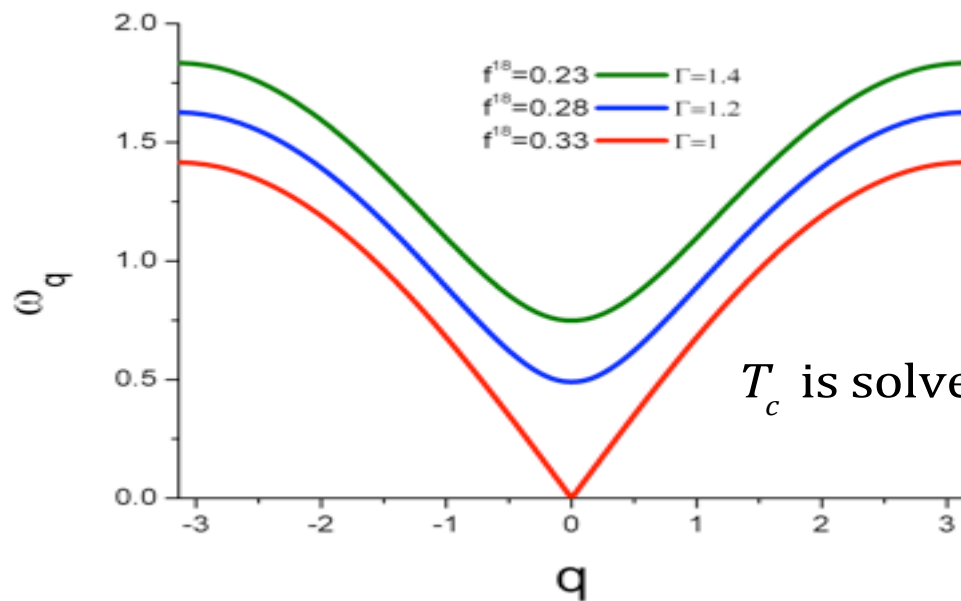


*Rowley et al,
Nature Phys.10, 367 (2014)*



$$\omega_q = \sqrt{\Gamma(y, n_e) - \cos q}$$

Superconducting pairing mediated by the ferro-electric softmode



T_c is solved from

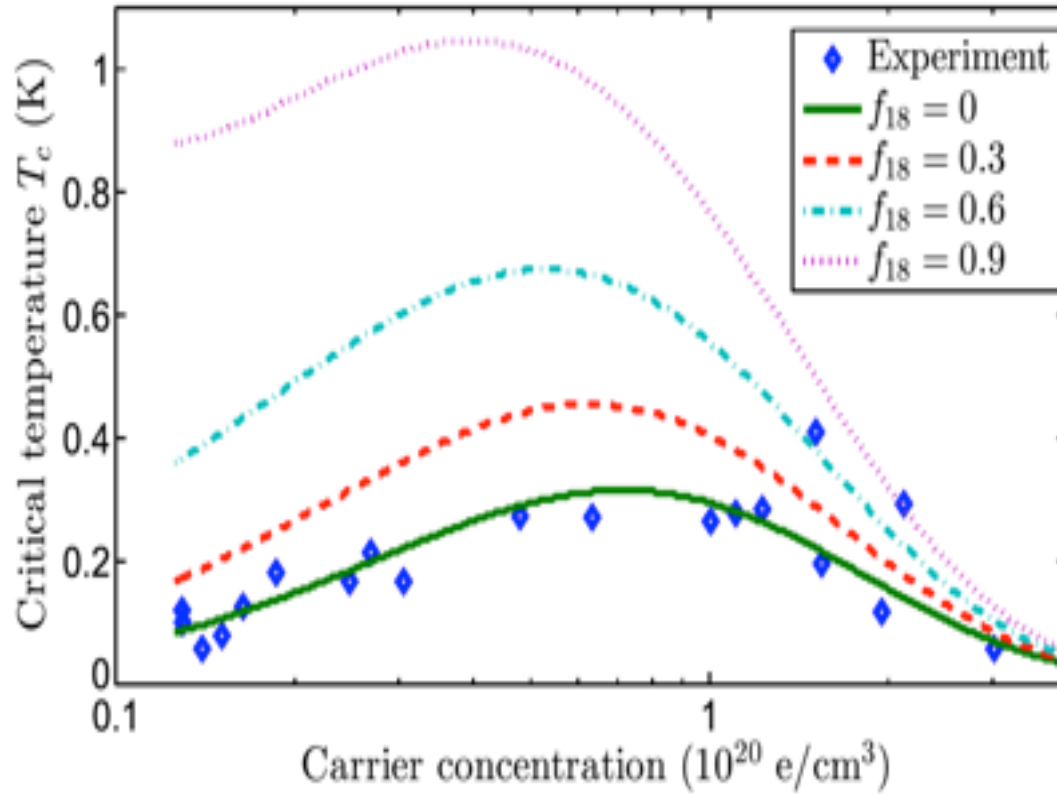
$$\omega_q = \sqrt{\Gamma'} \sqrt{\Gamma' - \cos q}$$

$$\Gamma = 1 + A(f_{QCP}^{18} - f^{18})$$

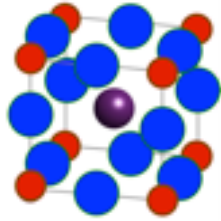
$$\Gamma' = \Gamma + BT_F + CT_F^2$$

$$\int \frac{\rho(\varepsilon)}{\varepsilon} \tanh\left(\frac{\varepsilon}{2T_c}\right) d\varepsilon = \frac{1}{\langle 1/\omega_q \rangle}$$

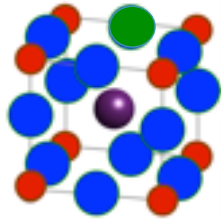
Prediction: very strong isotope effect: $-10 \times BCS$



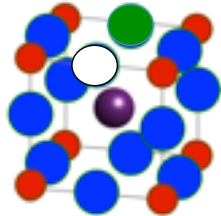
Preparation of $\text{SrTi}(\text{O}^{16}_{1-y}\text{O}^{18}_y)_{3-\delta}$ samples



SrTiO_3 single crystals
**Insulator & Quantum
Paraelectric**

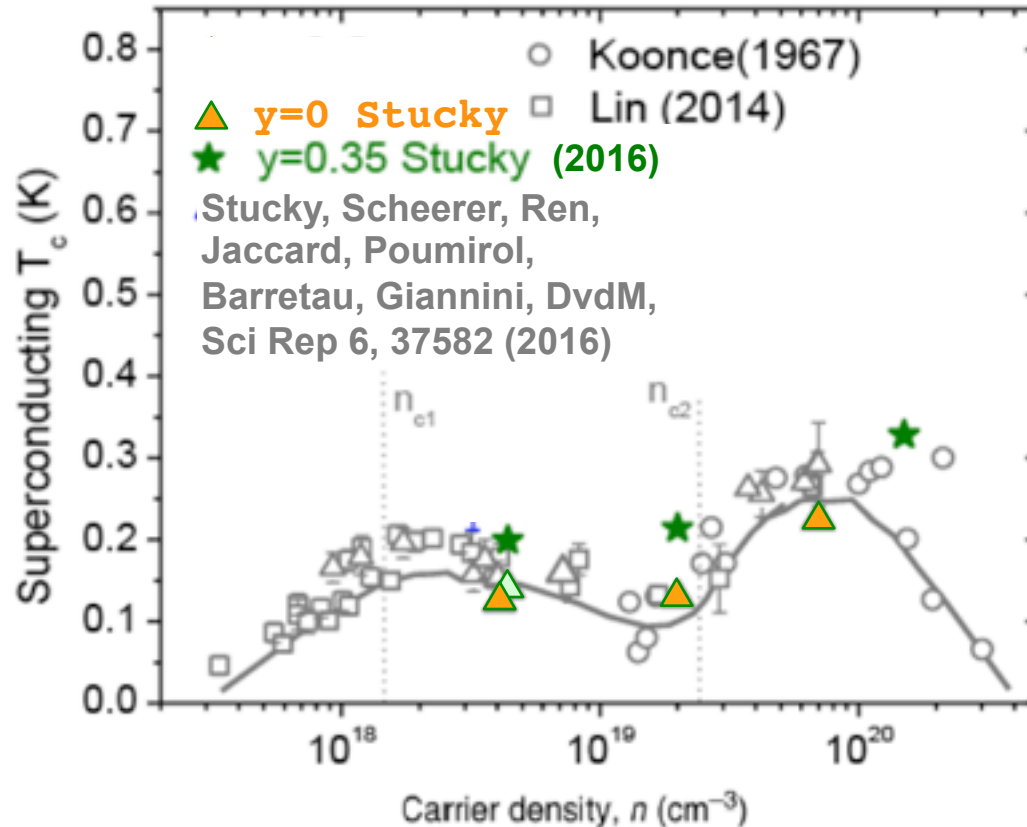
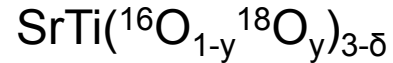


Annealing in ^{18}O atmosphere
 $\rightarrow \text{SrTi}(\text{O}^{16}_{1-y}\text{O}^{18}_y)_3$
**Insulator &
Ferroelectric for $y > 0.33$**



Annealing in vacuum
 $\rightarrow \text{SrTi}(\text{O}^{16}_{1-y}\text{O}^{18}_y)_{3-\delta}$ ($10^{-5} < \delta < 10^{-2}$)
Metal & Superconductor

Electron doped SrTiO₃: Superconductivity

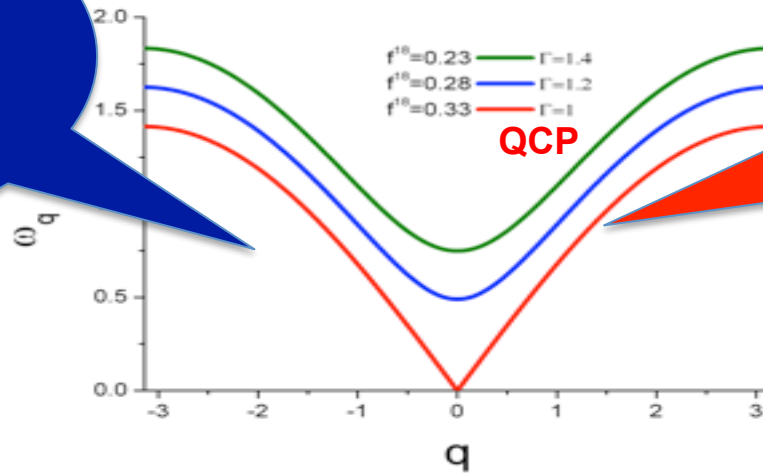


Pairing in doped STO mediated by soft ferro-electric phonons



The predicted anomalous isotope effect on T_c has been verified experimentally, but.....

The quantum critical phonons are transverse optical (TO)



Problem: Electrons with $k \approx 0$ don't have the required coupling to TO phonons

The conundrum of the pairing mechanism in SrTiO_3



~~Proposal: Intravalley and intervalley phonons - ML Cohen, PR 134 (1964)~~

Problem: Single valley bandstructure - LF Mattheiss, PRB 6 (1972)

~~Proposal: Folded zone boundary phonons - J Appel, PR 180 (1969)~~

~~Proposal: Acoustic phonons - Th Jarlborg PR B61 (2000)~~

Problem: Small Fermi surface $\Rightarrow \omega(2k_F) \ll \omega_D$

~~Proposal: Ferro electric soft modes - JM Edge et al., PRL 115 (2015)~~

Problem: Vanishing e-ph coupling - J. Ruhman and P. A. Lee, arXiv:1901.11065

~~Proposal: Longitudinal optical phonons - LP Gorkov, PNAS 113 (2016)~~

Problem: Anti-adiabatic limit $\Rightarrow$ Screening of the Coulomb repulsion but no overscreening

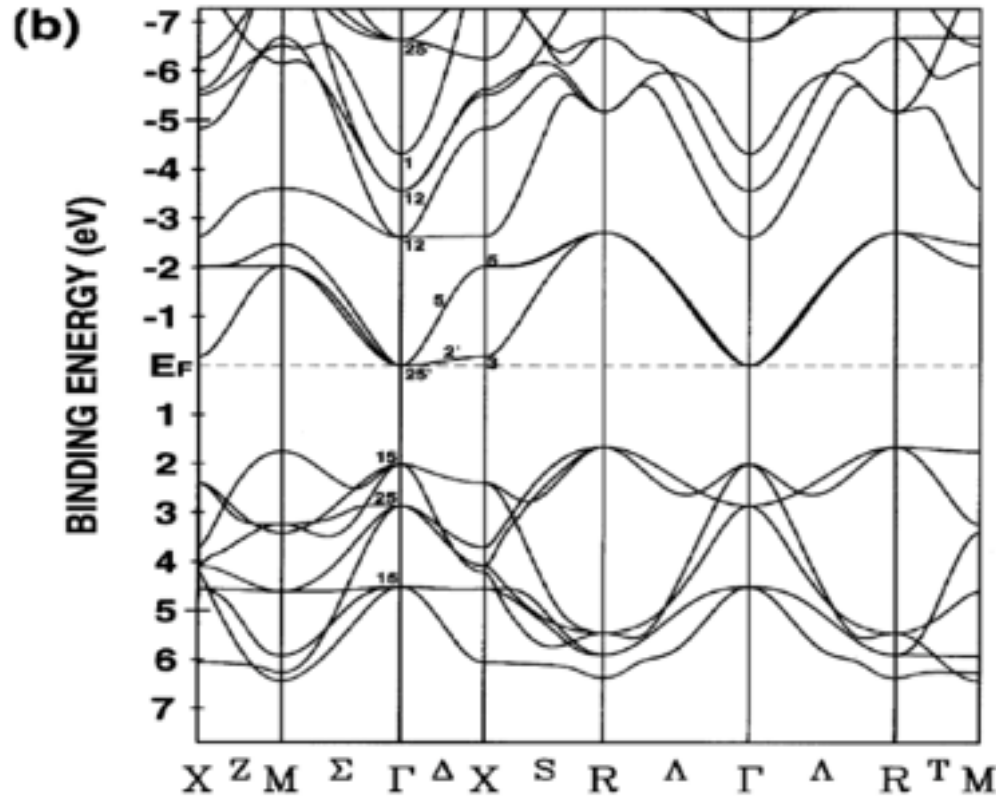
Proposal: Bi-phonons - KL Ngai, PRL 32 (1974)

Problem: Paper did not draw much attention

The papers citing *Ngai, PRL 32 (1974)*

DvdM, F. Barantani & W. Rischau, Phys Rev R 1, 013003 (2019)
Noad et al., Phys Rev B 94, 174516 (2016)
Boschker et al., Sci Rep 5, 12309 (2015)
Jourdan, Blumer, Adrian, Eur Phys J B 33, 25 (2003)
Enaki, Ereemeev, New J Phys 4, 80 (2002)
Gervais, Materials Science & Engineering Reports 39, 29 (2002)
Gervais et al., Phys Rev B 47, 8187 (1993)
Bussmann-Holder, Ferroelectrics 150, 25 (1993)
Sugai, Phys Rev B 45, 7577 (1992)
Allen, Mitrovic, Solid State Phys 37, 1 (1982)
Baratoff, Binnig, Physica B & C 108, 1335 (1981)
Takada, J Phys Soc Jpn 49, 1267 (1980)
Binnig et al., Phys Rev Lett 45, 1352 (1980)
Gregory et al., Phys Rev B 19, 1039 (1979)
Karakozov, Maksimov, Zh Eksp Teor Fiz 74, 681 (1978)
Toyoda, Ferroelectrics 8, 691 (1974)
Ngai, Ganguly, Ruvalds, Phys Rev B 10, 3280 (1974)

SrTiO₃ Band Structure

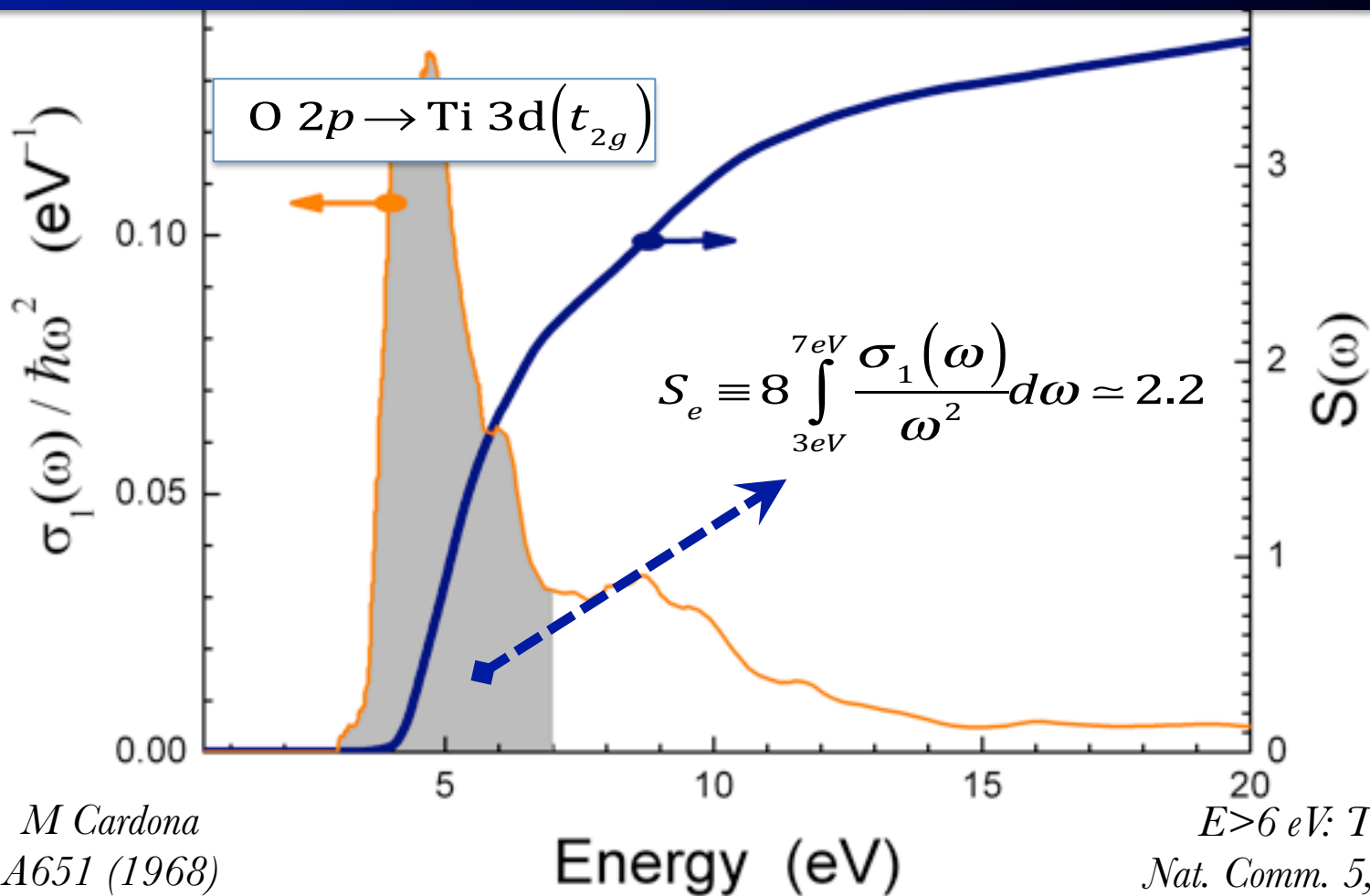


} Ti 3d(e_g) {x²-y², z²}

} Ti 3d(t_{2g}) {xy, yz, zx}

} O 2p

Electronic Polarizability: O2p & Ti3d



$E < 6$ eV: M Cardona
PR 40, A651 (1968)

$E > 6$ eV: TC Asmara et al
Nat. Comm. 5, 3663 (2014)

Oscillator strength of the $O2p - Ti3d$ transition



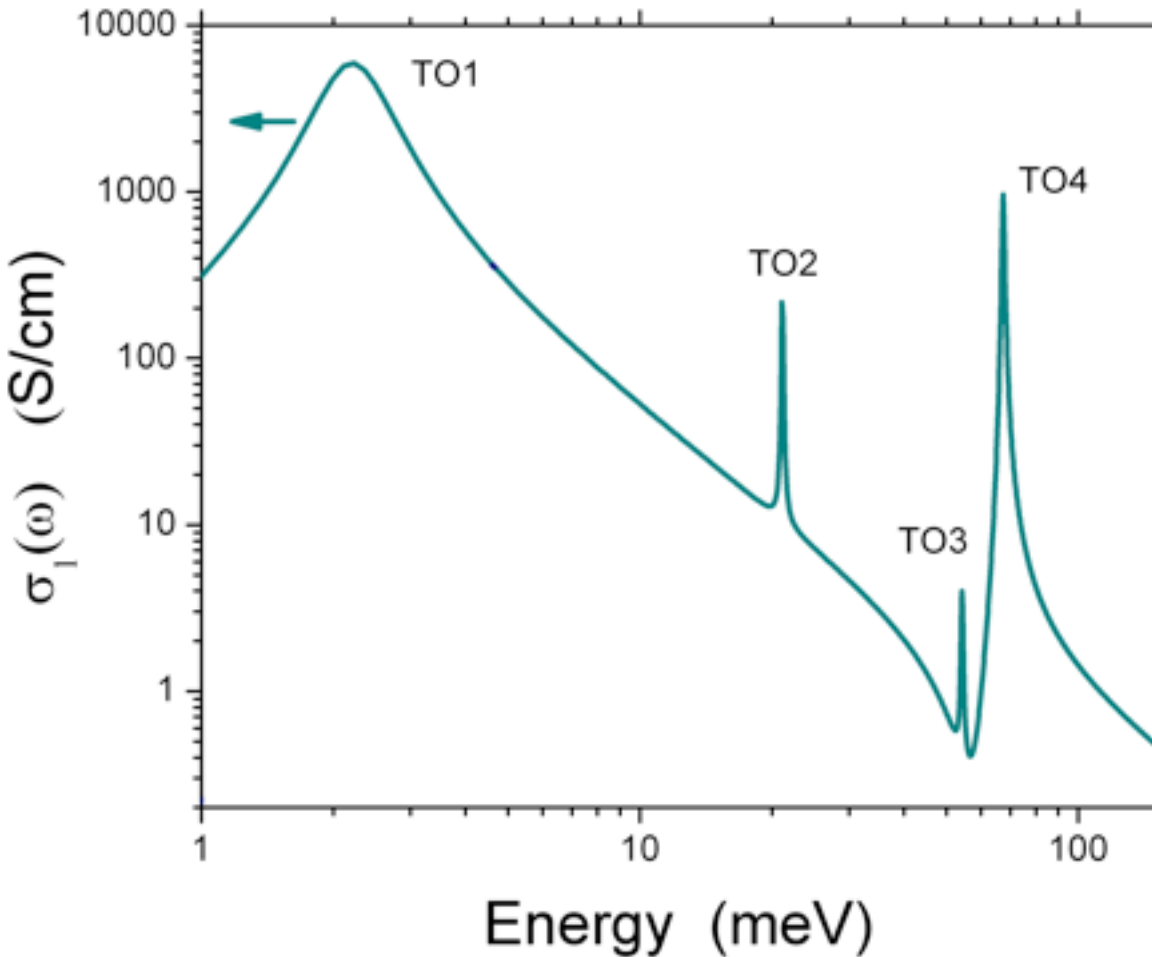
$$\varepsilon(0) = 1 + S_{ph} + S_e$$

Displacement operator:
$$\begin{cases} \hat{x}_e = a_e (\hat{d}^\dagger \hat{p} + \hat{p}^\dagger \hat{d}) \\ a_e \equiv \text{length scale of the } p \rightarrow d \text{ transition} \end{cases}$$

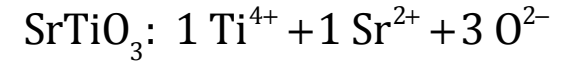
Linear response theory:
$$S_e = \frac{8\pi e^2}{\hbar} \frac{n_{p,e} a_e^2}{\omega_e}$$

$$S_e \simeq 2.2 \ ; \ \omega_e \simeq 5 \text{ eV} \Rightarrow a_e \simeq 1 \text{ \AA}$$

Transverse optical phonons

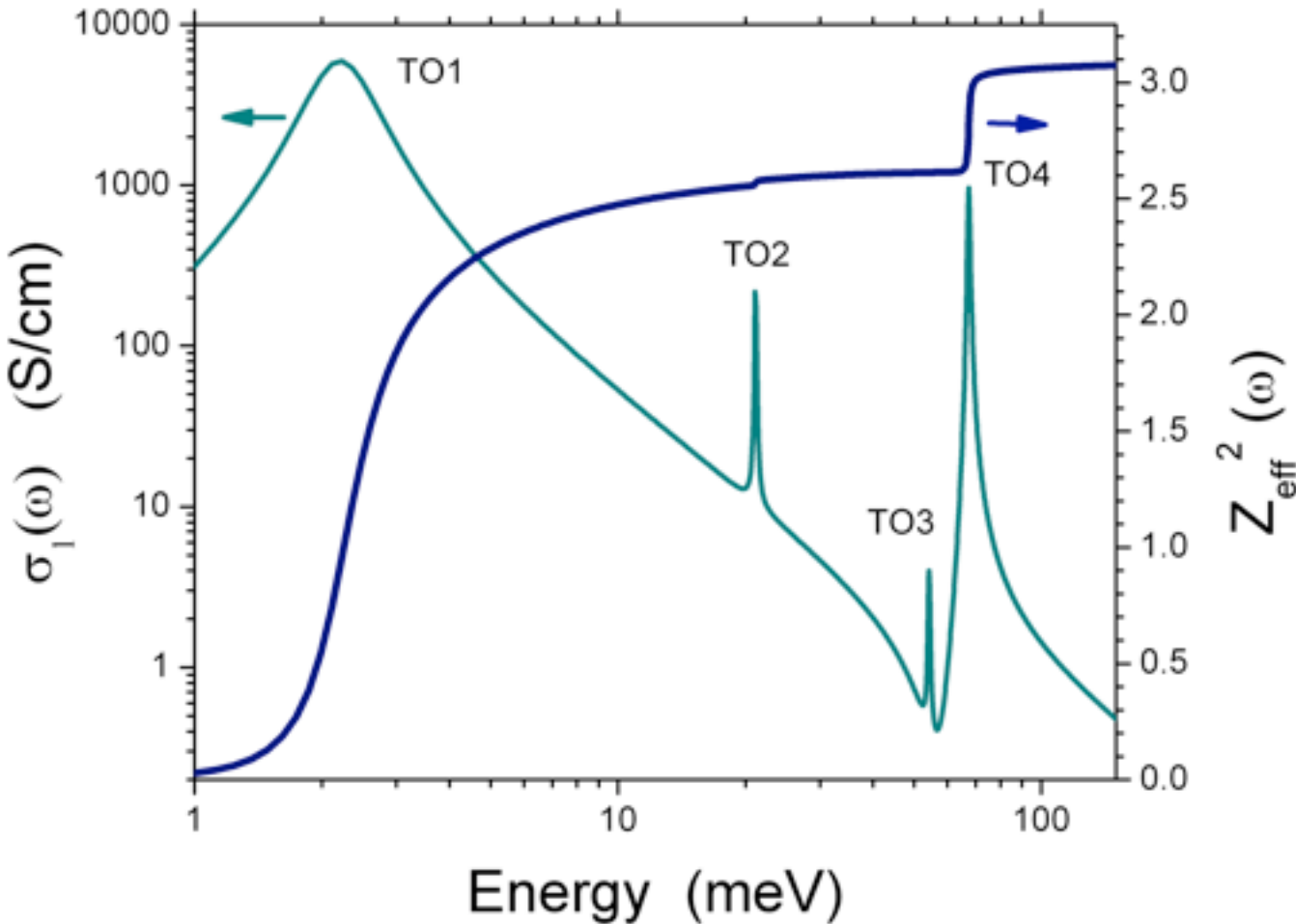


$$\int_0^{\infty} \sigma_1(\omega') d\omega' = Z_{eff}^2 \sum_j \frac{\pi N_j q_j^2}{2m_j V_u}$$



Ionic crystal: $Z_{eff}^2 = 1$

Transverse optical phonons



$$Z_{\text{eff}}^2(\omega) = \frac{\int_0^\omega \sigma_1(\omega') d\omega'}{\sum_j \frac{\pi N_j q_j^2}{2m_j V_u}}$$



Transverse effective charge: $Z_{\text{eff}}^2 = 3.1 \neq 1$

Organic metals: "Charged Phonon"

MJ Rice, NO Lipari & S Strässler, PRL 39, 1359 (1977) (organic metals)

SrTiO₃ :

W Zhong, RD King-Smith & D Vanderbilt, PRL 72, 3618 (1994)

Physics: Coupling of a vibrational oscillator to a collective charge mode

Coupling to transverse optical phonons



$$H = \frac{p_e^2}{2\tilde{m}_e} + \frac{\tilde{m}_e \omega_e^2 x_e^2}{2} + \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2 x_n^2}{2} - \gamma x_e x_n$$

Classical solution for the vibrational conductivity ($\omega \ll \omega_e$)

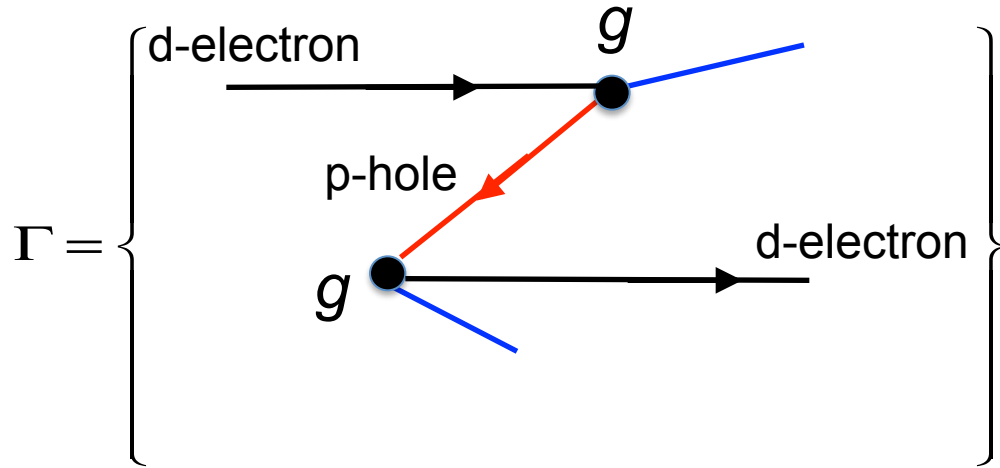
$$\sigma_n(\omega) = \frac{\omega_{p,n}^2}{4\pi} \frac{i\omega Z_{eff}^2}{\omega^2 - \tilde{\omega}_n^2} \quad ; \quad \gamma = (Z_{eff}^2 - 1) \tilde{m}_e \omega_e^2 \quad \Rightarrow \gamma \approx 6 \text{ eV} / \text{\AA}^2$$

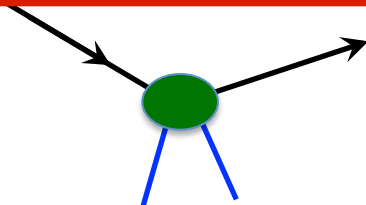
Quantum formulation of the same system:

$$\hat{H} = \varepsilon_p \hat{p}^\dagger \hat{p} + (\varepsilon_p + \hbar\omega_e) \hat{d}^\dagger \hat{d} + \hbar\omega_n \hat{a}^\dagger \hat{a} - g(\hat{d}^\dagger \hat{p} + \hat{p}^\dagger \hat{d})(\hat{a}^\dagger + \hat{a})$$

$$g = \gamma a_e \sqrt{\frac{\hbar}{2m_n \tilde{\omega}_n}} \quad ; \quad a_e \approx 1 \text{ \AA} \quad \Rightarrow g \approx 0.5 \text{ eV}$$

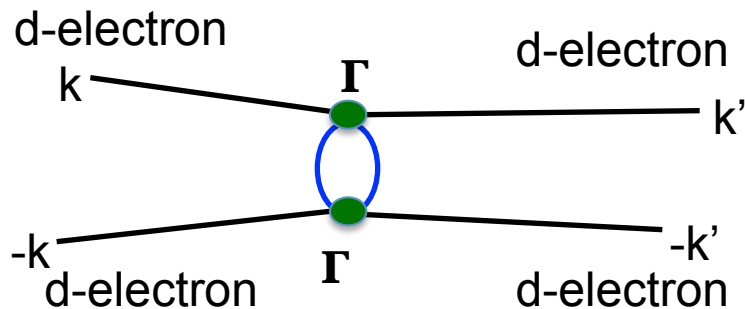
Coupling to transverse optical phonons



$$\Gamma = \frac{g^2}{\hbar\omega_e} =$$


$$\omega_e \approx 5 \text{ eV} ; g \approx 0.5 \text{ eV} \Rightarrow \Gamma \approx 70 \text{ meV}$$

Electron pairing mediated by TO bi-phonons



$$\lambda_{2ph} = \frac{\Gamma^2 D^*(\epsilon_F)}{\hbar \tilde{\omega}_n}$$

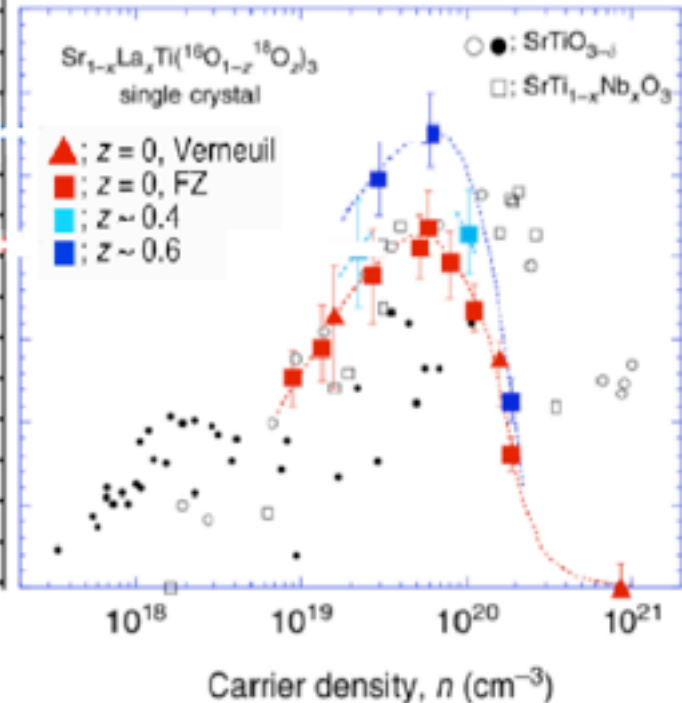
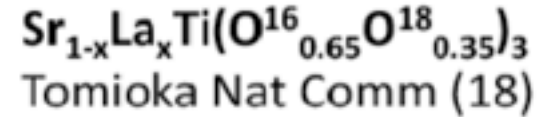
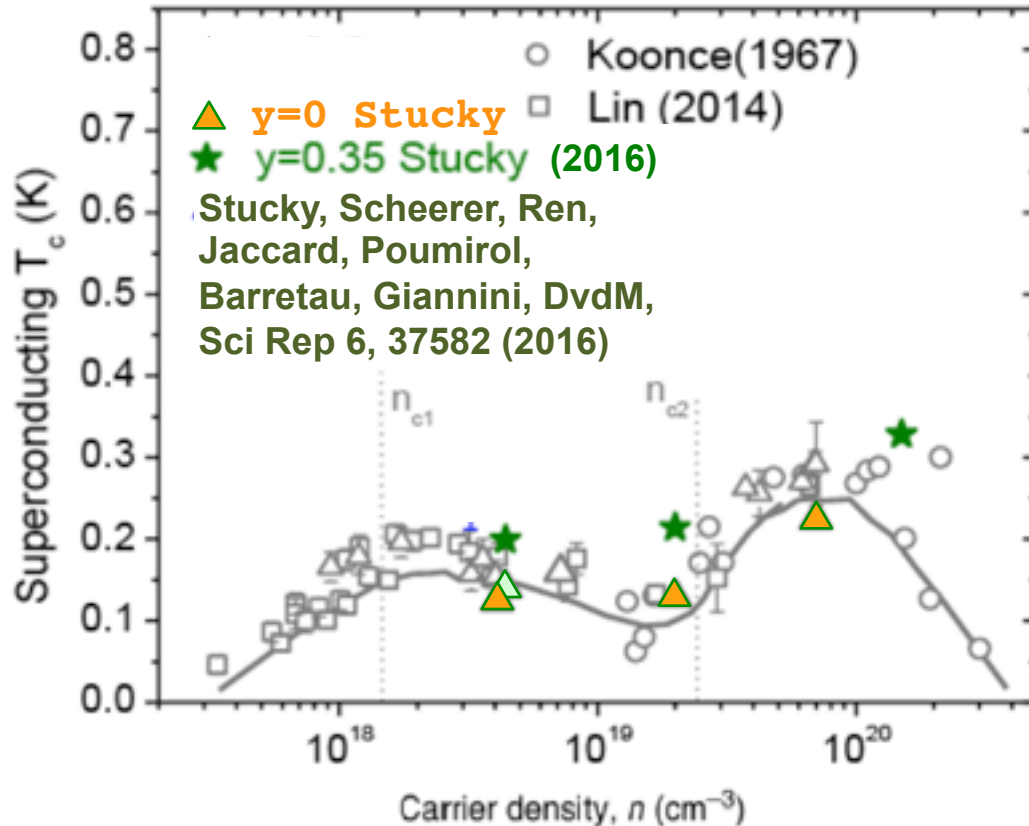
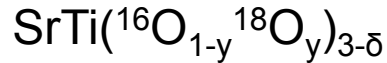
$$\Gamma \approx 70 \text{ meV} ; \hbar \tilde{\omega}_n \approx 12 \text{ meV} ; D^*(\epsilon_F) \leq 0.8 \text{ eV}^{-1} \Rightarrow \lambda_{2ph} \leq 0.28$$

DvdM et al, PRB 84, 205111 (2011):

Experimental T_c 's: **$0.1 < \lambda < 0.2$**

Transport data: **$0.1 < \lambda < 0.4$**

Meanwhile the ^{18}O isotope experiments continued



Pairing in doped STO mediated by 2 soft ferro-electric phonons



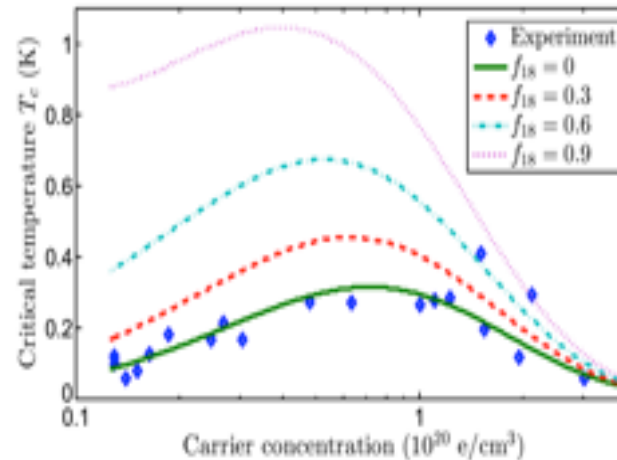
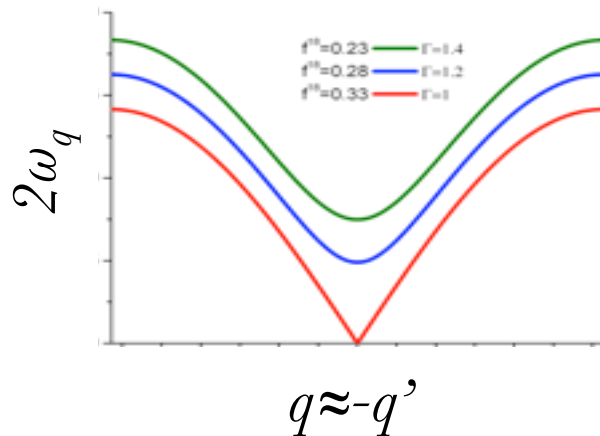
2-phonon pairing: $(k, -k) \rightarrow (k+q+q', -k-q-q')$

k and $k+q$ are (almost) at the Fermi surface.

Small doping $\Rightarrow q+q' \approx 0$

$$\Rightarrow \omega_q \approx \omega_{q'}$$

**The phonons are the same ones as in *JM Edge et al, PRL 115, 247002 (2015)*.
Instead of $\omega_q : (\omega_q ; \omega_{-q})$ pairs. Relaxed cinematic constraints on q .**





1) Coupling of O2p-Ti3d & TO1

a) Pump TO1, probe O2p-Ti3d

b) Pump O2p-Ti3d, probe TO1

2) Superconductors of the Second Kind

a) Whack TO1, probe $\epsilon(\omega)$ at low frequencies

b) Whack O2p-Ti3d, probe $\epsilon(\omega)$ at low frequencies

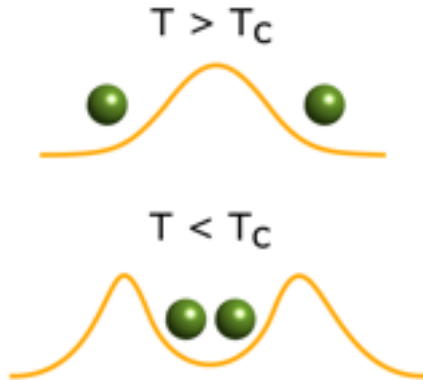
Conclusions



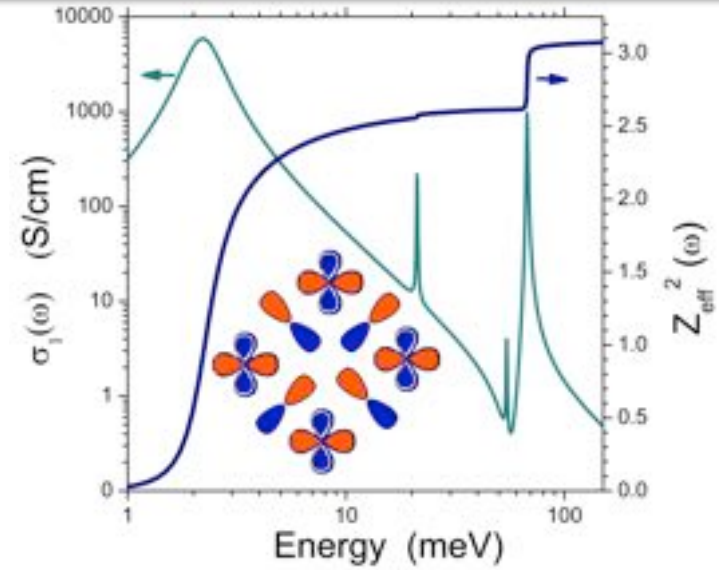
Pairing by transverse optical phonons requires exchange of bi-phonons instead of single phonons

The coupling constant can be calculated from the charged phonon effect in undoped STO.

Since the charged phonon effect is anomalously strong in STO, the corresponding e-ph coupling constant is very large. Back to Ngai, PRL 32 (1974).



The bi-phonons that mediate the pairing are transverse polarized soft ferro-electric modes: Prone to anomalous isotope effects, as in Edge et al, PRL 115, 247002 (2015).



DvdM, F Barantani, CW Rischau, *Physical Review Research* **1**, 013003 (2019)