Electron-hole fluctuations driving the charge density wave phase transition in $TiSe_2$

Claude Monney

Dynamics of correlated materials
Fritz-Haber Institute, Berlin

Electronic Structure and Electron Spectroscopies, Kiev, May 2013

Acknowledgements

Electron spectroscopy group (Fribourg, CH):
H. Cercellier[1], G. Monney, E. Schwier and P. Aebi

Theory:
H. Beck (Neuchâtel, CH)

G. Monney

P. Aebi

H. Beck

TiSe$_2$ samples:
H. Berger and L. Forro (EPFL, CH),
J. Marcus (Institut Néel, Grenoble, F),
A. Titov (Institute of Metal Physics, Ekateringburg (R)

[1] Now in: Institut Néel, Grenoble (F)

Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

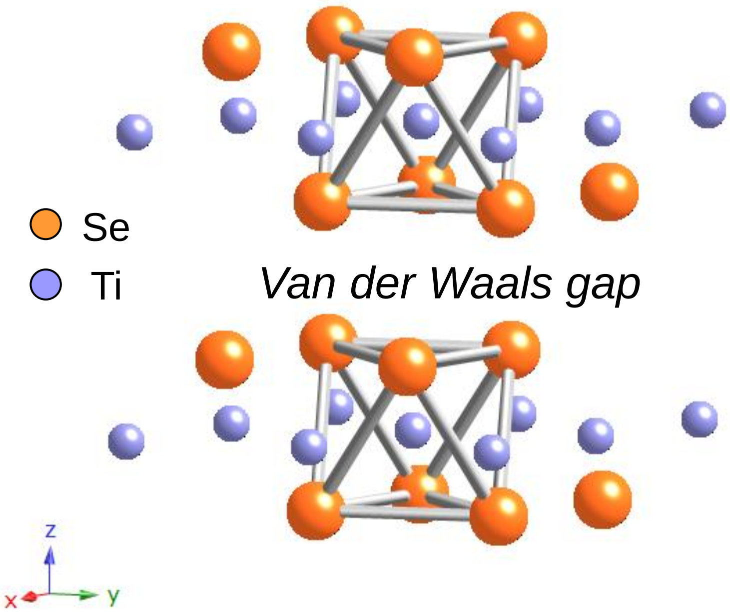
Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

Physical properties of $TiSe_2$: structure

Layered compound with 1*T* structure

Threefold symmetry around z-axis

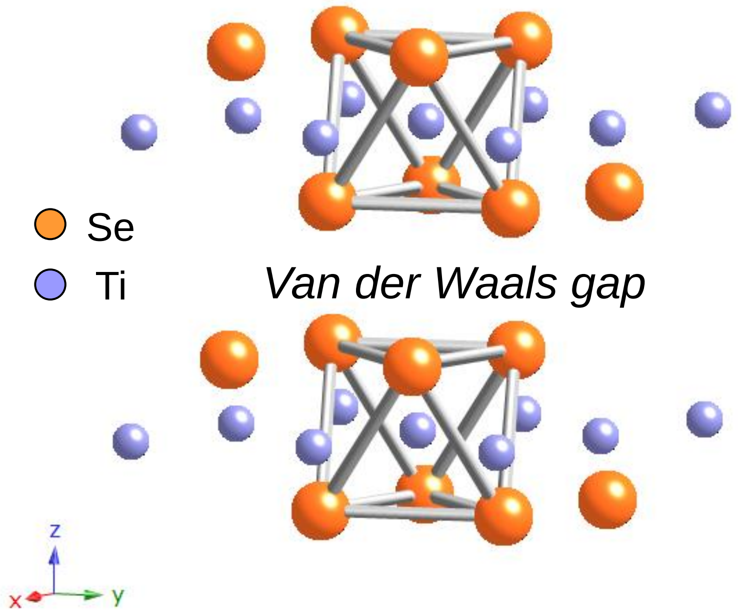


Ti in octahedral coordination

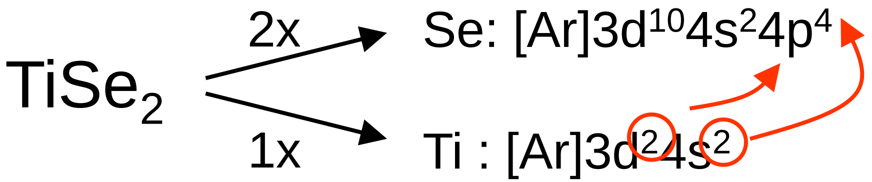
Physical properties of $TiSe_2$: structure

Layered compound with 1*T* structure

Threefold symmetry
around z-axis



Ti in octahedral
coordination



$TiSe_2$

2x

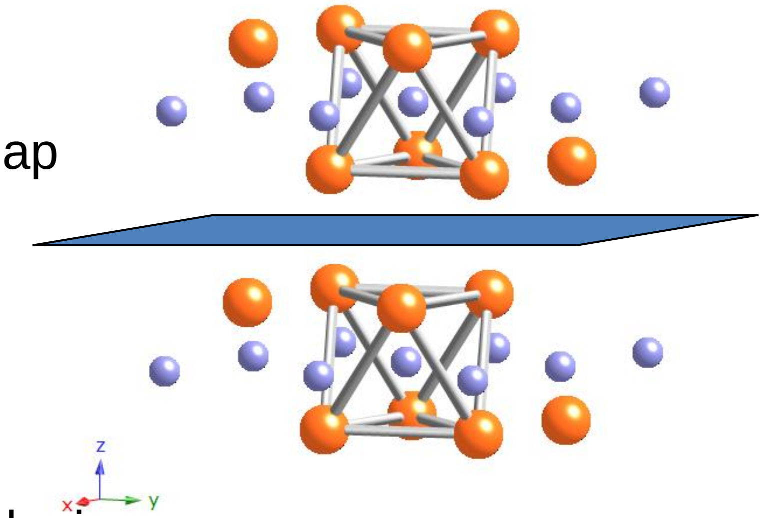
Se: $[Ar]3d^{10}4s^{2}4p^{4}$

1x

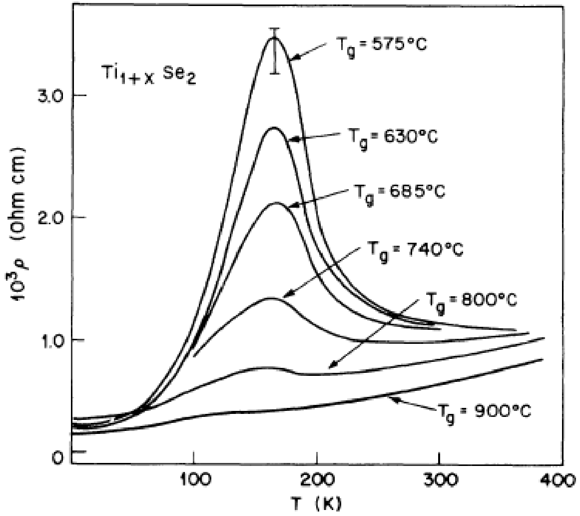
Ti : $[Ar]3d^{2}4s^{2}$

Effect of doping : intercalated compounds

Van der Waals gap



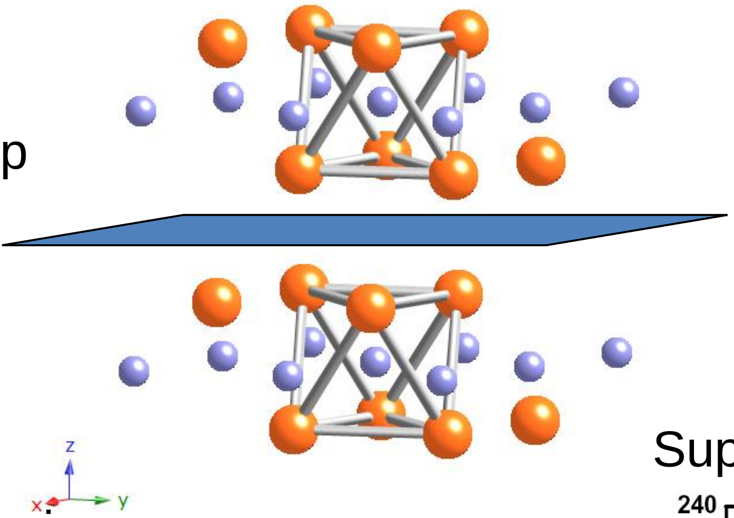
Ti overdoping
Intercalation compound



Di Salvo et al., PRB 14 (1976)

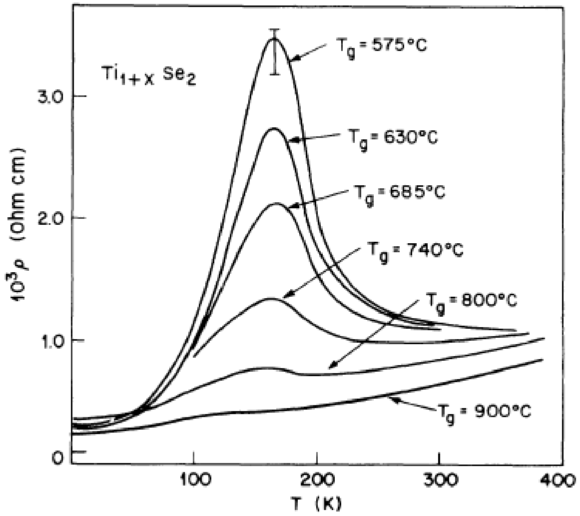
Effect of doping : intercalated compounds

Van der Waals gap



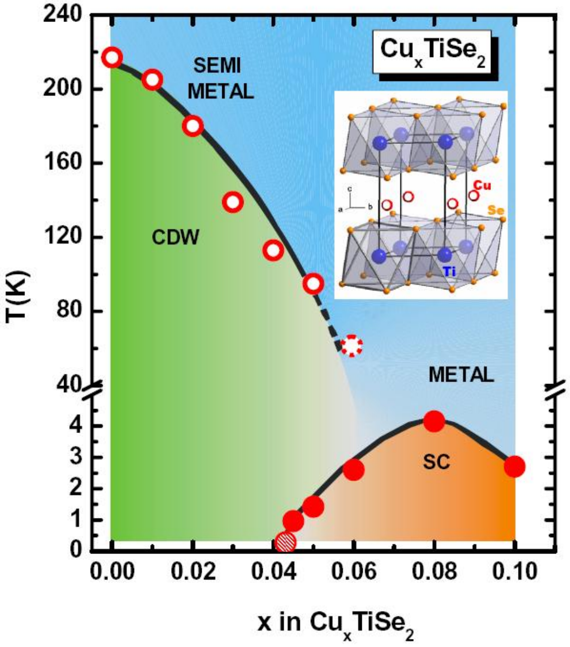
Ti overdoping
Intercalation compound

Di Salvo et al., PRB 14 (1976)



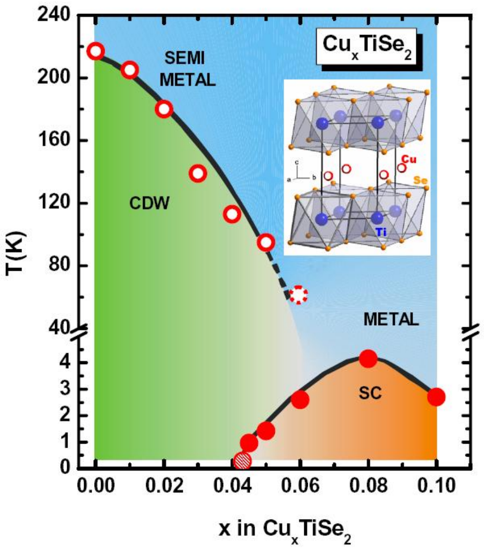
Superconducting Cu_xTiSe_2

Morosan *et al.*, Nature Phys. **2** (2006)

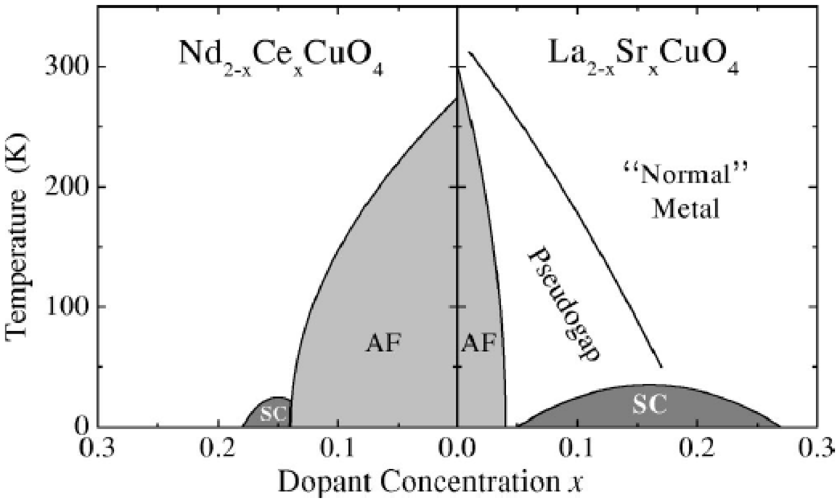


Universality of phase diagrams?

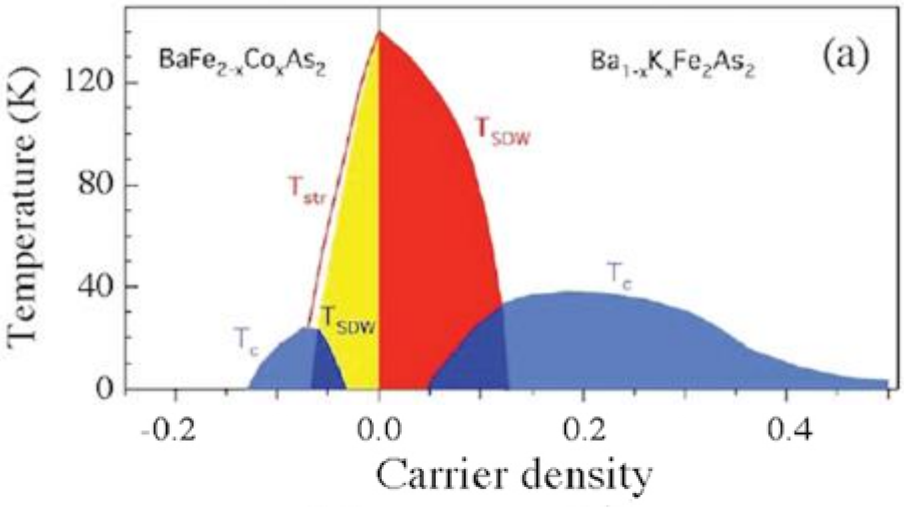
- Similar phase diagrams in quasi 2D materials
- Superconductivity develops in the proximity of an ordered phase (CDW, SDW, …)



Morosan *et al.*, Nature Phys. **2** (2006)

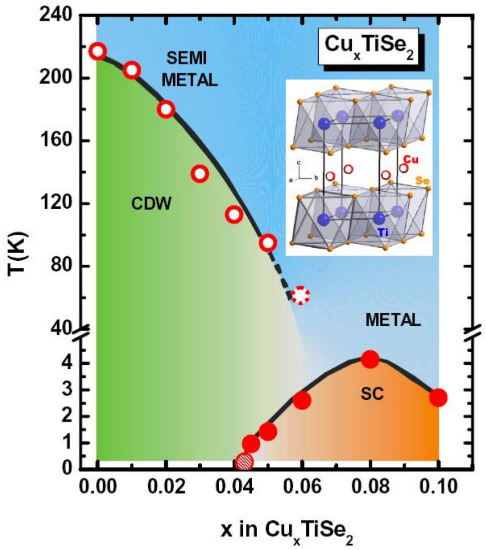


Damascelli et al., Rev. Mod. Phys. (2003)



Richard et al., Rep. Prog. Phys. (2011)

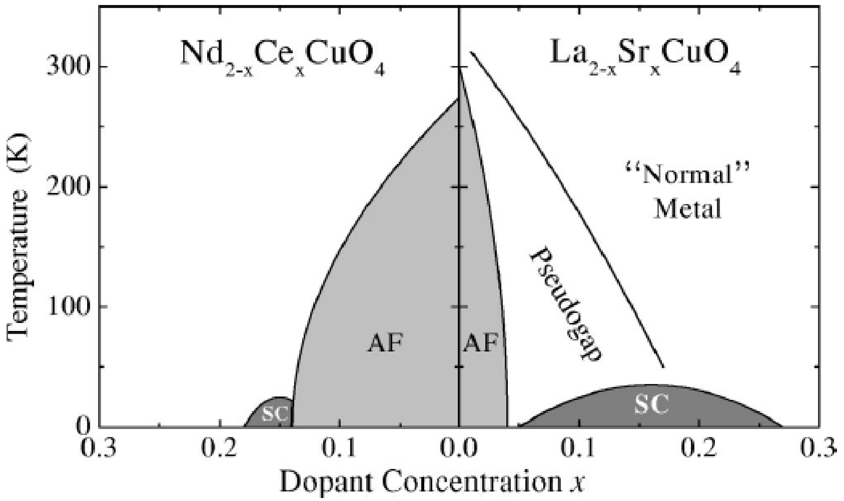
Universality of phase diagrams?



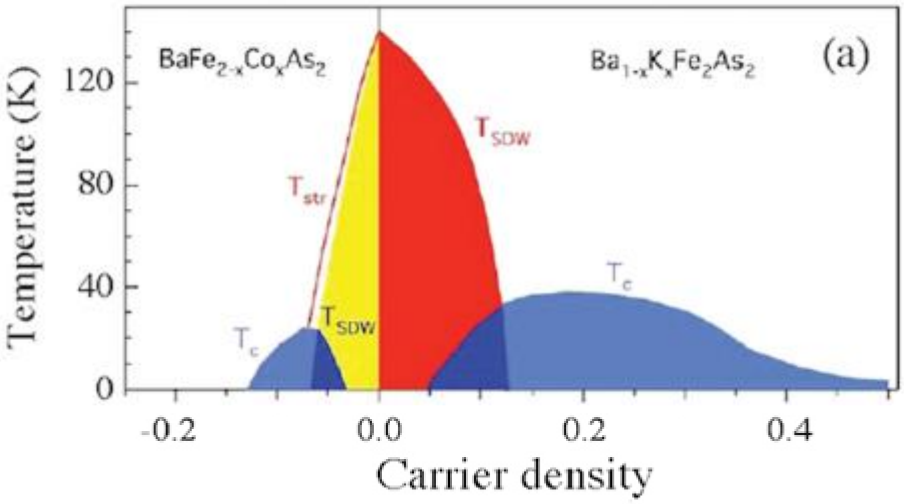
Morosan *et al.*, Nature Phys. **2** (2006)

- Similar phase diagrams in quasi 2D materials
- Superconductivity develops in the proximity of an ordered phase (CDW, SDW, …)

We need to investigate more the nature of CDW to better understand the competition(?) CDW & SC



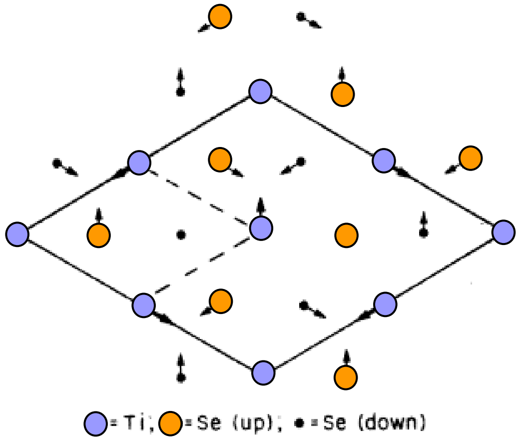
Damascelli et al., Rev. Mod. Phys. (2003)



Richard et al., Rep. Prog. Phys. (2011)

Physical properties of $TiSe_2$: transport

Phase transition at T_c~ 200 K: charge density wave (CDW)

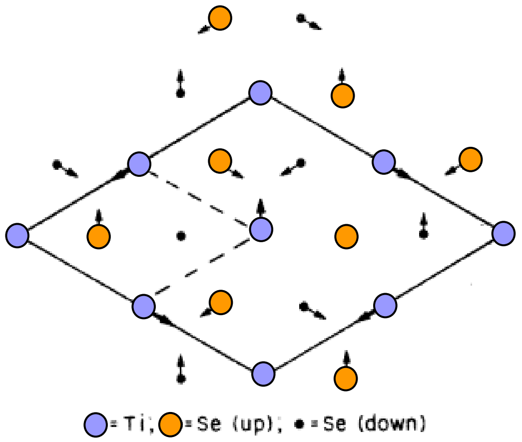


Distortion
(1x1x1) => (2x2x2)
with small atomic
displacements (~ 0.08)

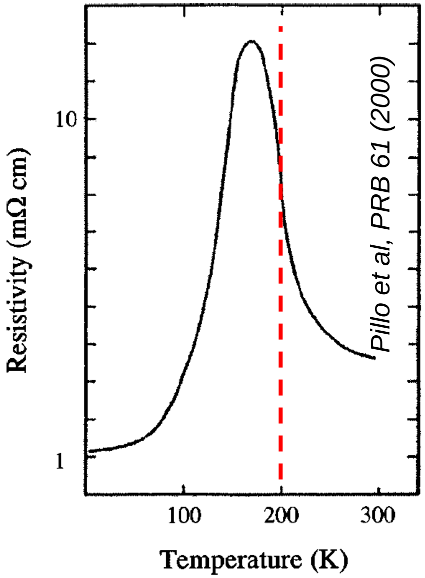
*according to Di Salvo et al, PRB **14**, 4321 (1976)*

Physical properties of $TiSe_2$: transport

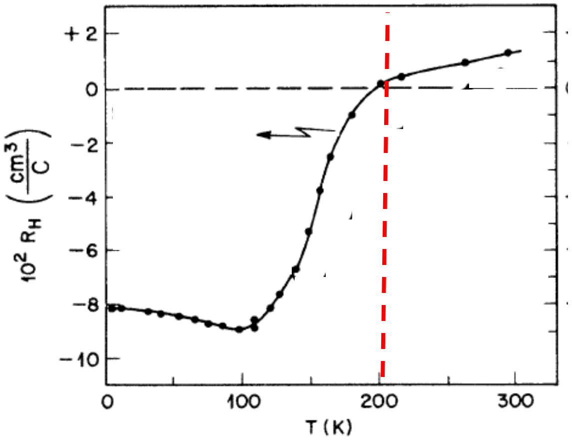
Phase transition at T_c~ 200 K: charge density wave (CDW)



Distortion
(1x1x1) => (2x2x2)
with small atomic
displacements (~ 0.08)



Pillo et al, PRB 61 (2000)



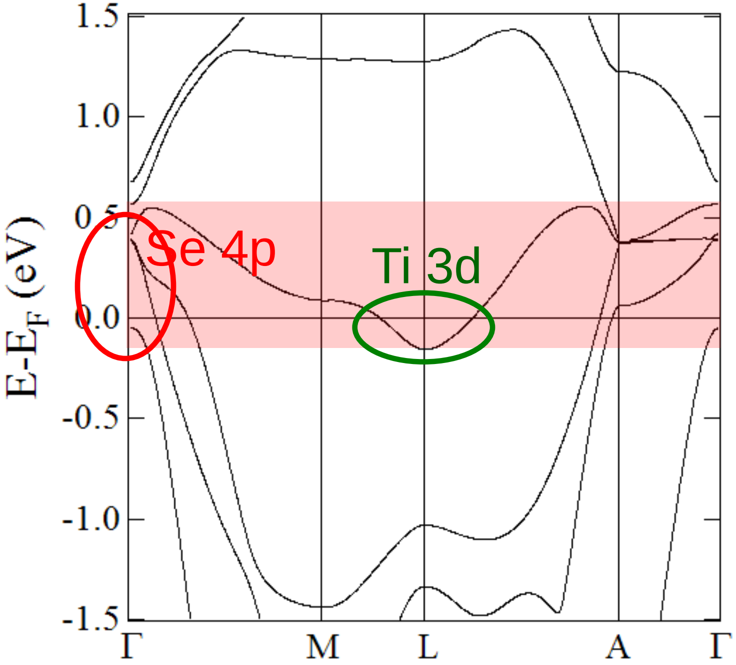
Anomalous transport

Carrier density 10^{21} cm^{-3}
« bad metal »

Dominant carriers:
holes at RT
electrons at low temperatures

*according to Di Salvo et al, PRB **14**, 4321 (1976)*

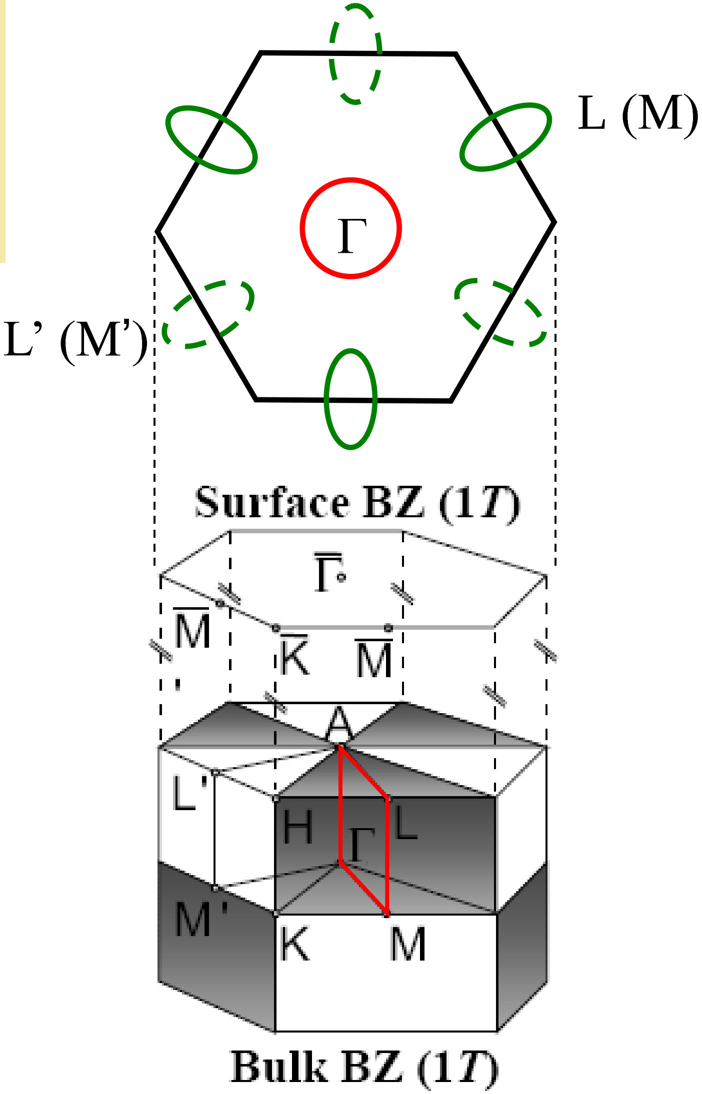
Physical properties of $TiSe_2$:electronic structure



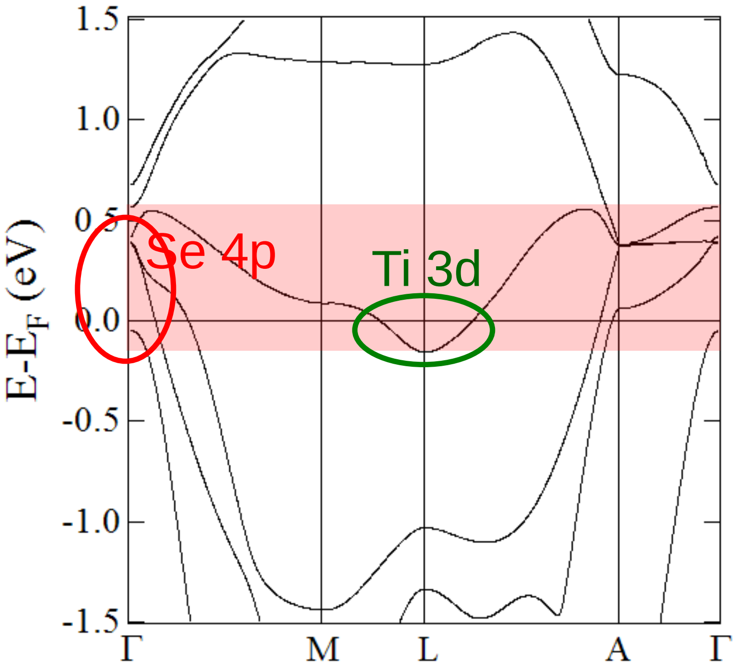
DFT : metal

4p-3d overlap
~ 500 meV

Fermi surface



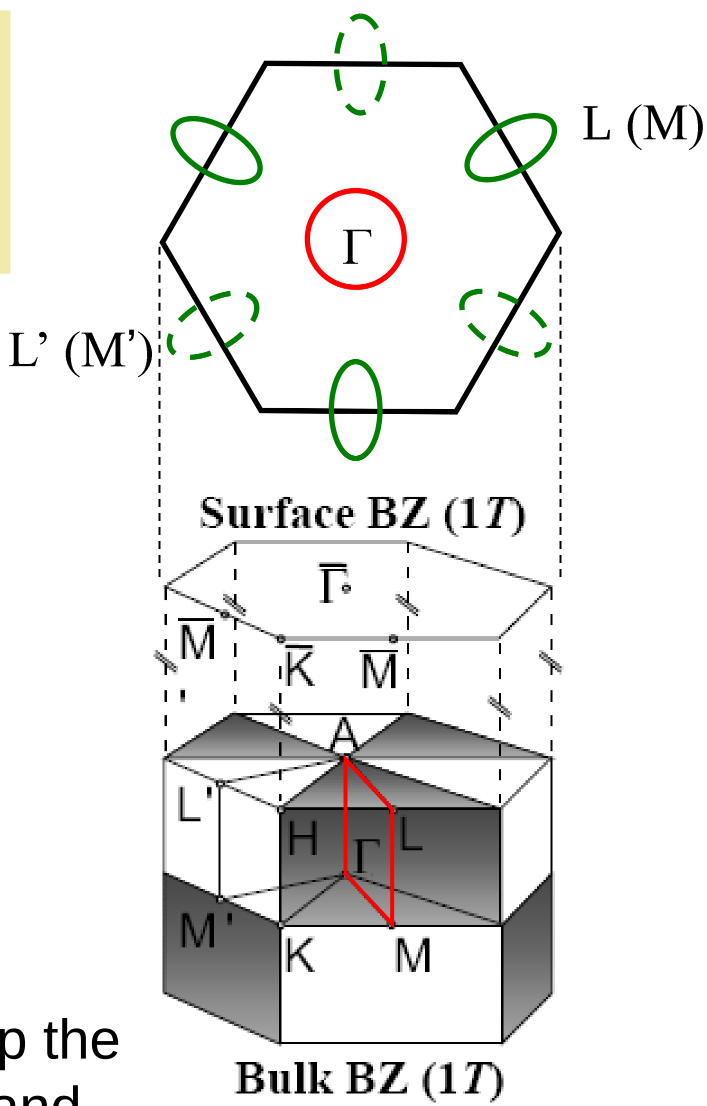
Physical properties of $TiSe_2$:electronic structure



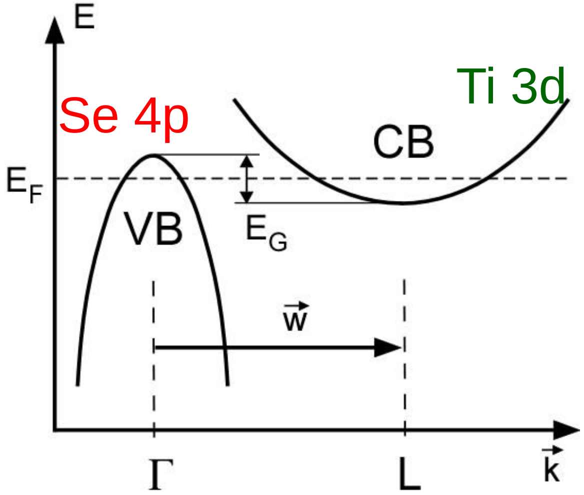
DFT : metal

4p-3d overlap
~ 500 meV

Fermi surface



simplified
model for
the bands
near E_F

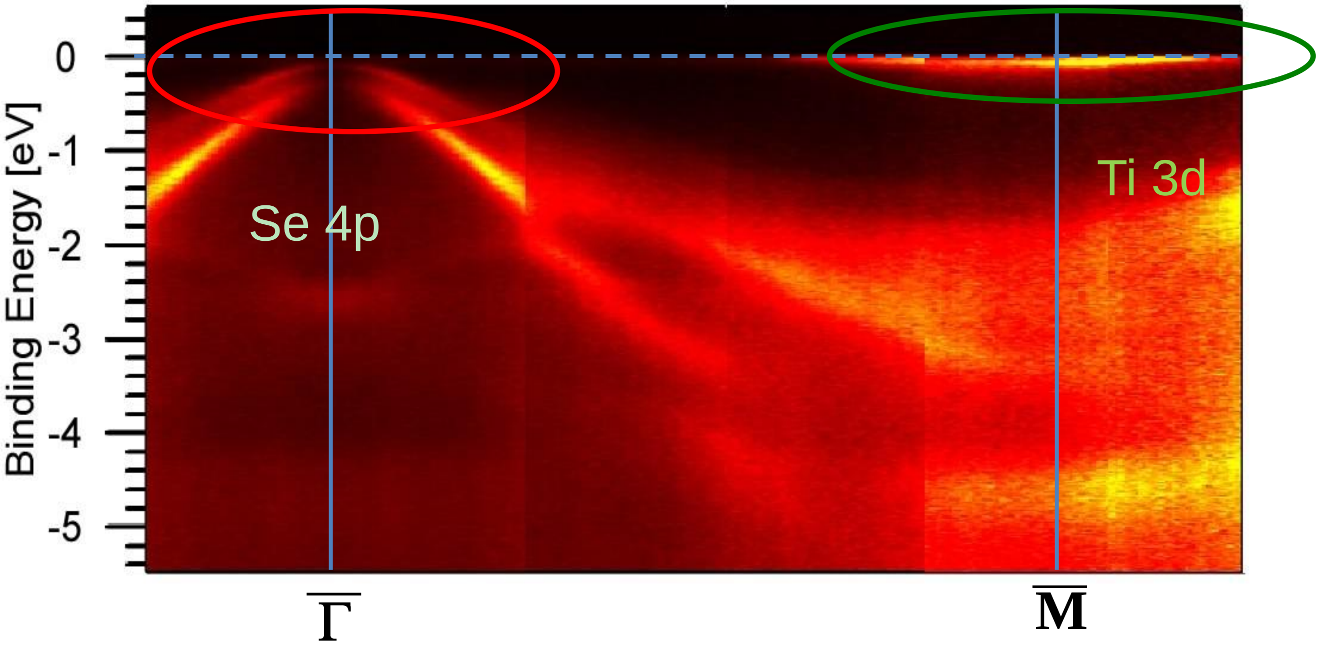


In the model, we keep the topmost valence band

Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

ARPES on 1*T*-TiSe$_2$: normal phase



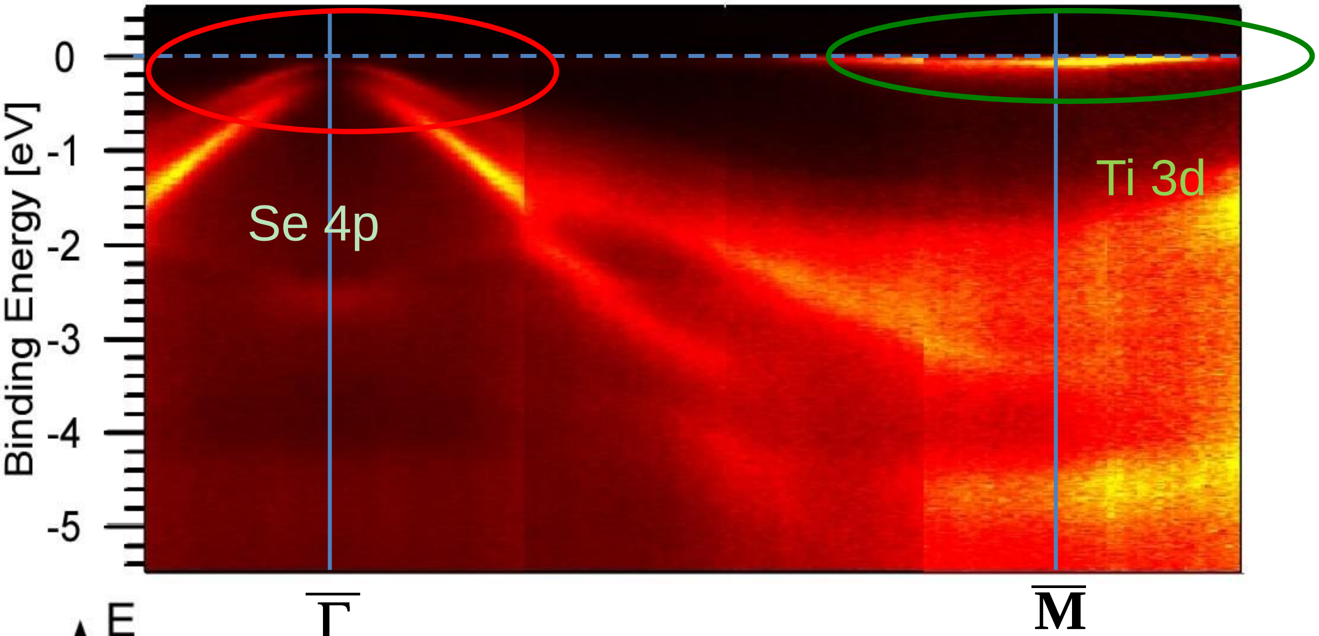
hν = 100 eV

T=300 K

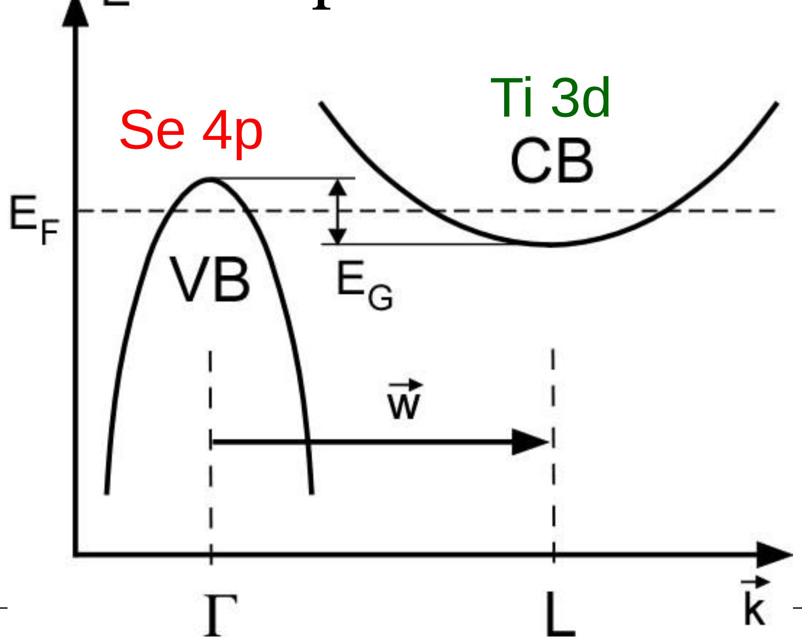
hν = 21.2 eV

Fermi surface

ARPES on 1*T*-TiSe$_2$: normal phase



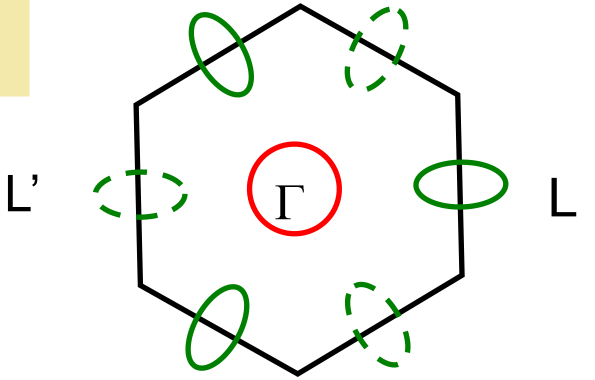
hν = 100 eV
T=300 K



From experiment
E_G < 500 meV

SO splitting of
valence band

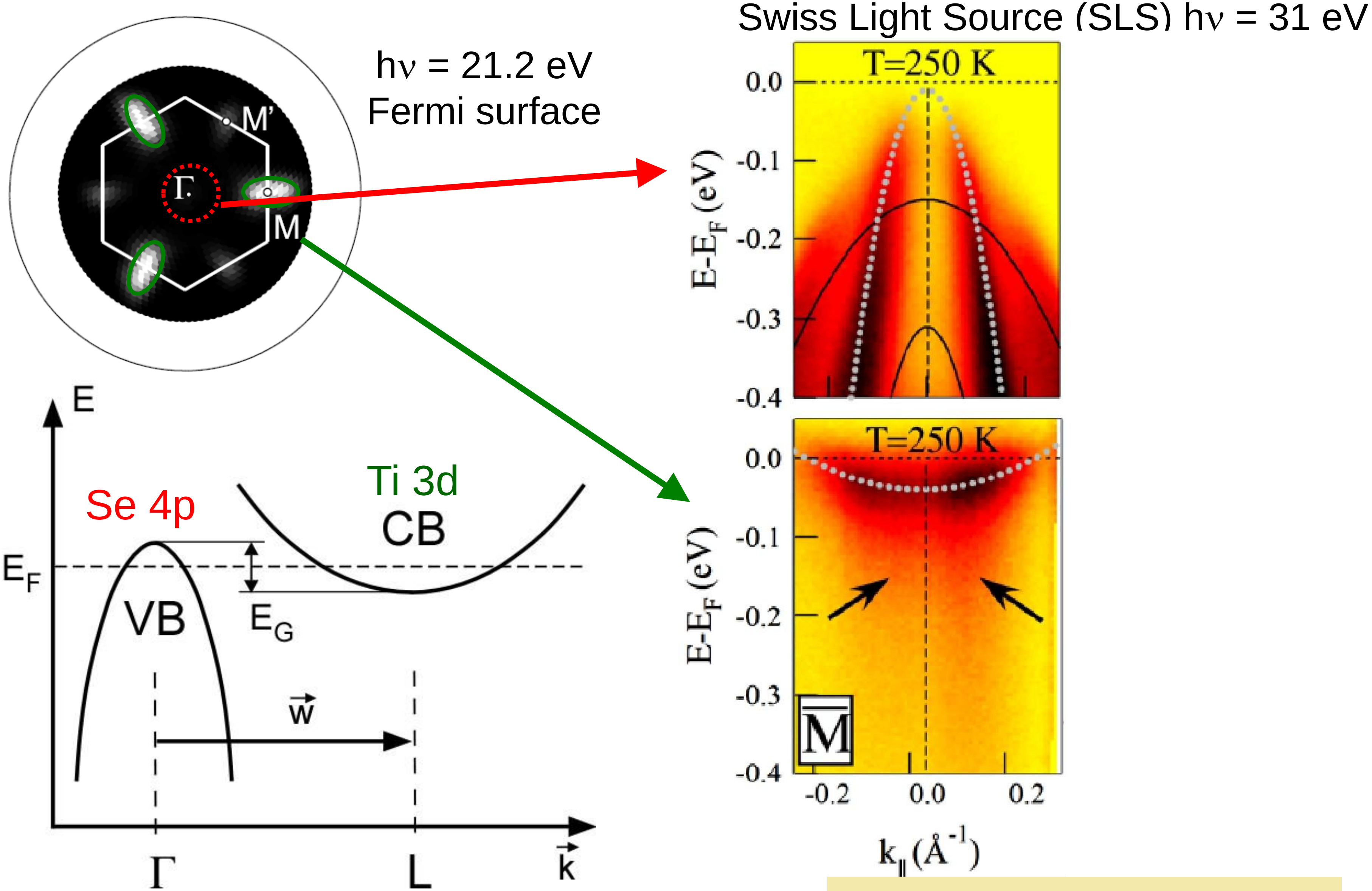
hν = 21.2 eV
Fermi surface



ARPES on 1*T*-TiSe$_2$:   and L

hν = 21.2 eV
Fermi surface

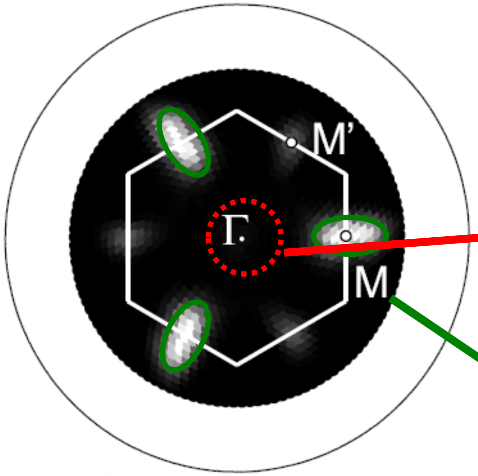
Swiss Light Source (SLS) hν = 31 eV



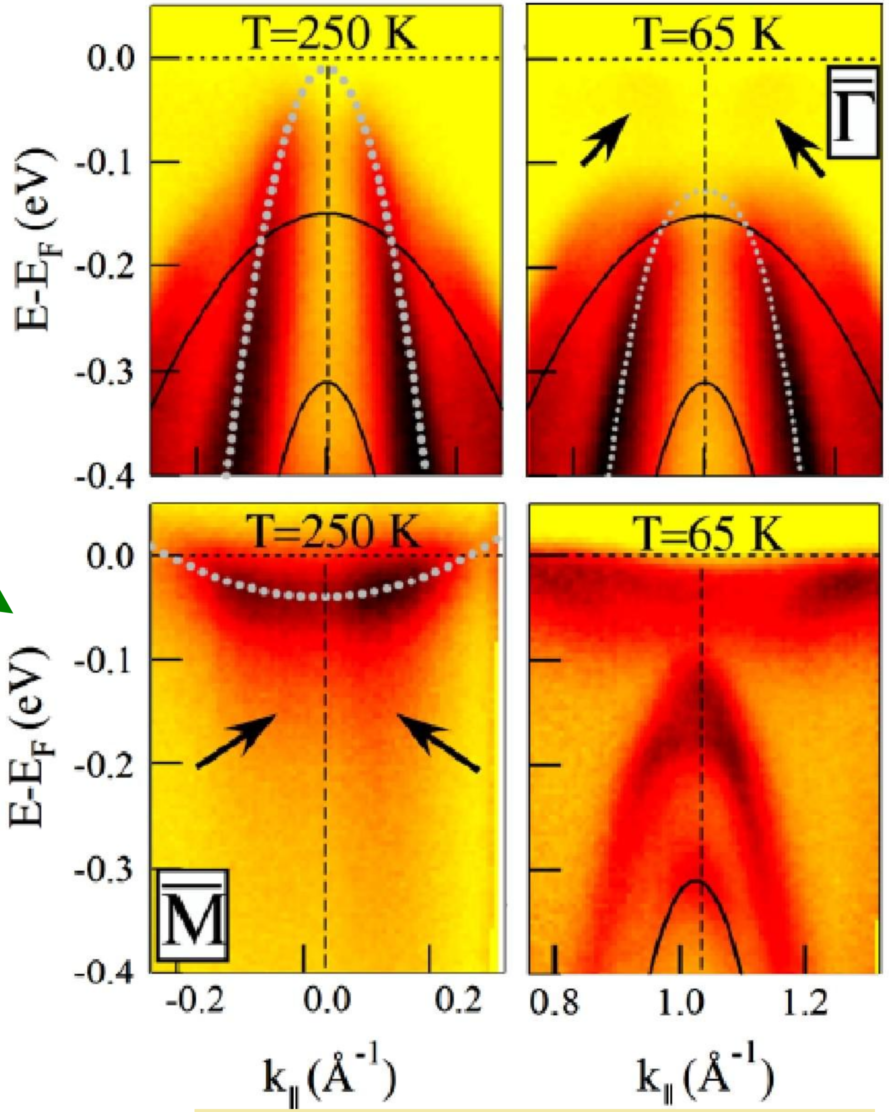
Overlap deduced: ~ 70 meV

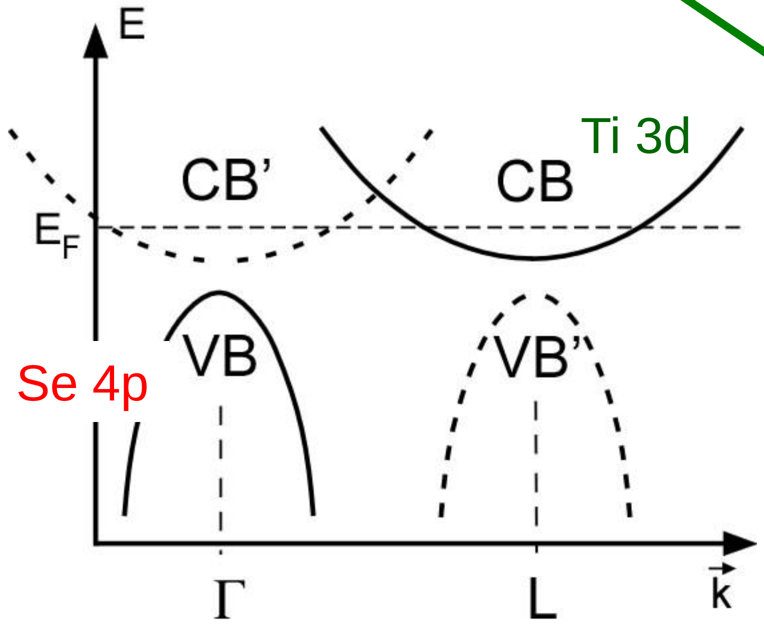
ARPES on 1*T*-TiSe$_2$: and L

hν = 21.2 eV
Fermi surface



Swiss Light Source (SLS) hν = 31 eV





Below the T$_c$: PLD *and* **CDW** phase

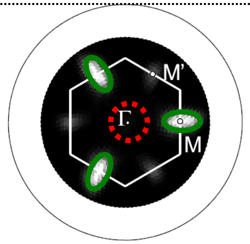
Overlap deduced: ~ 70 meV

Origin of the CDW transition

Ab-initio calculations ≠ Experiments

Models for the transition :

« Fermi surface nesting »



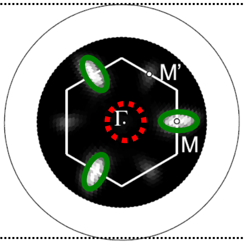
Fermi surface topology
not compatible

Origin of the CDW transition

Ab-initio calculations ≠ Experiments

Models for the transition :

~~« Fermi surface nesting »~~



Fermi surface topology
not compatible

Jahn-Teller effect

Single-electron picture
Band symmetry and degeneracy

Structural distortion
plays the major role

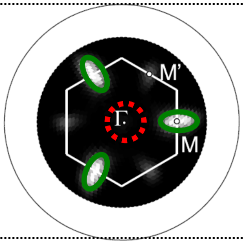
*Kidd et al, PRL **86**, 226402 (2002)*

Origin of the CDW transition

Ab-initio calculations ≠ Experiments

Models for the transition :

~~« Fermi surface nesting »~~



Fermi surface topology
not compatible

Jahn-Teller effect

Single-electron picture
Band symmetry and degeneracy

Structural distortion
plays the major role

*Kidd et al, PRL **86**, 226402 (2002)*

Excitonic insulator

Many-body physics

Purely electronic
Origin
Time-resolved exp

Spectroscopic signatures of an excitonic insulator phase? → ARPES

Spectroscopic signatures of an excitonic insulator phase? → Calculations

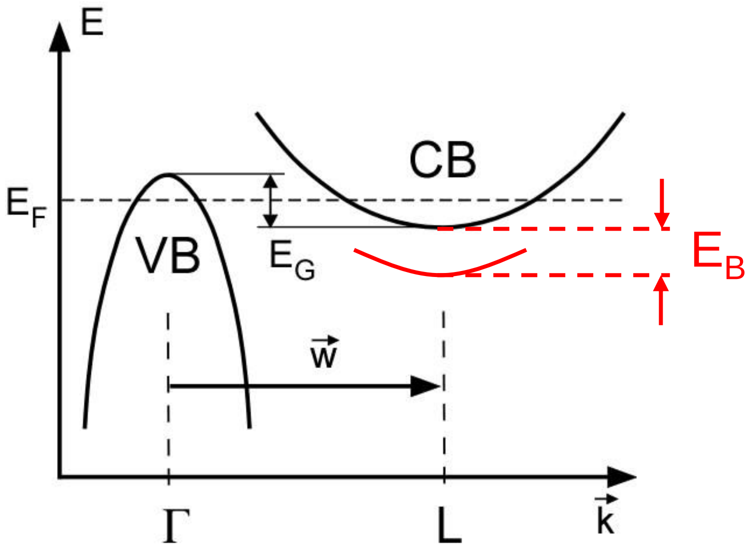
Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

The excitonic insulator

Model proposed in the mid-1960s:
L.V. Keldysh and Y.V. Kopaev, Sov. Phys. Solid State **6**, 2219 (1965)
D. Jérome, T.M. Rice and W. Kohn, Phys. Rev. **158**, 462 (1967)

Semimetal / semiconductor
indirect gap E_G~0
Small carrier density $E_B > |E_G|$



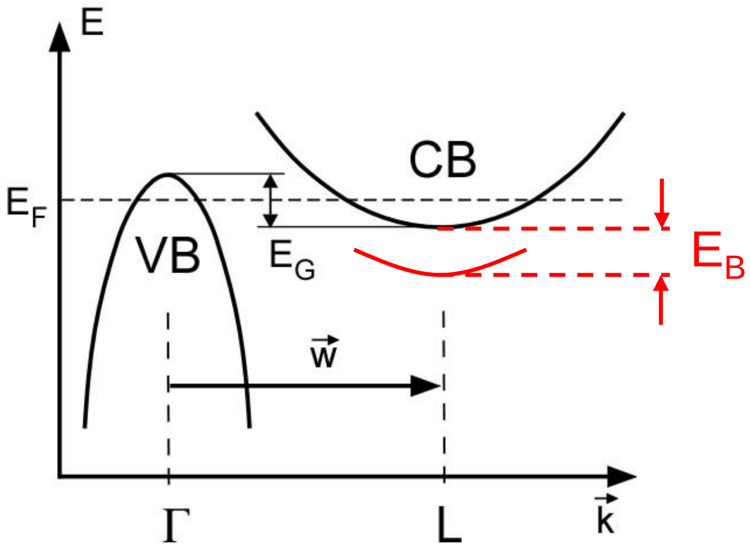
The excitonic insulator

Model proposed in the mid-1960s:
L.V. Keldysh and Y.V. Kopaev, Sov. Phys. Solid State **6**, 2219 (1965)
D. Jérome, T.M. Rice and W. Kohn, Phys. Rev. **158**, 462 (1967)

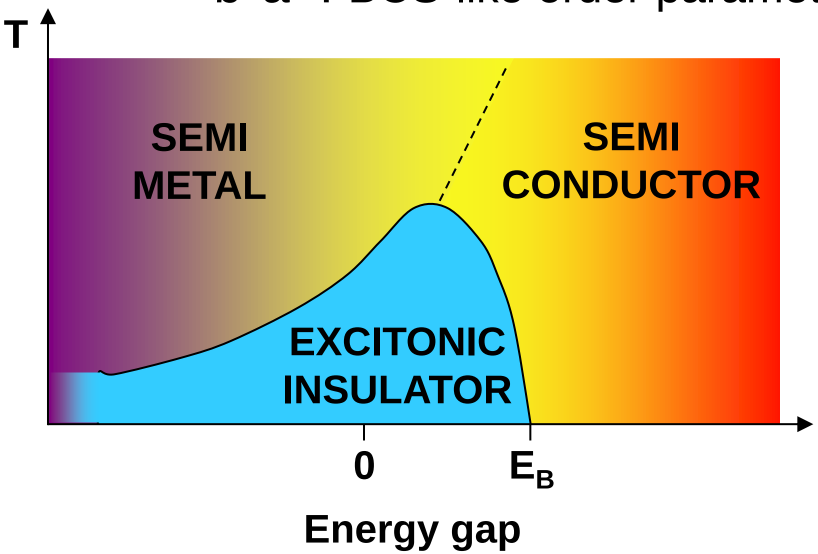
Semimetal / semiconductor
indirect gap $E_G \sim 0$
Small carrier density $E_B > |E_G|$

Instability

New ground state :
EXCITONIC INSULATOR
New periodicity



$\sim\langle b^{+}a\rangle$: BCS-like order parameter



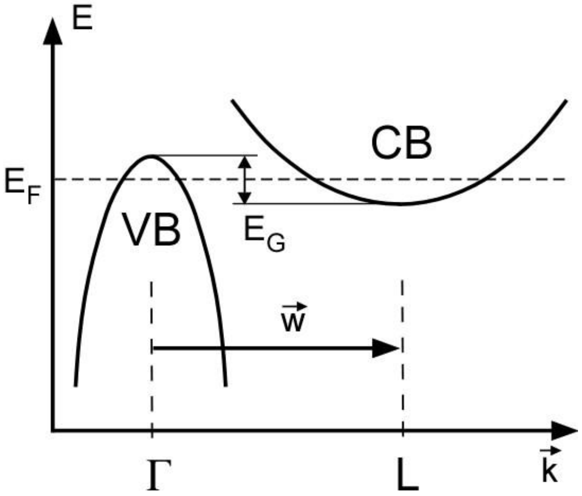
The excitonic insulator: a BCS-like model (mean field)

$$H = H_0 + W$$

$$H_0 = \sum_k \epsilon_a(k) a^+(k) a(k) + \sum_{k,w} \epsilon_b(k,w) b^+(k+w) b(k+w).$$

1-electron Hamiltonian

Valence band
Maximum at Γ



Conduction band
Minima at w

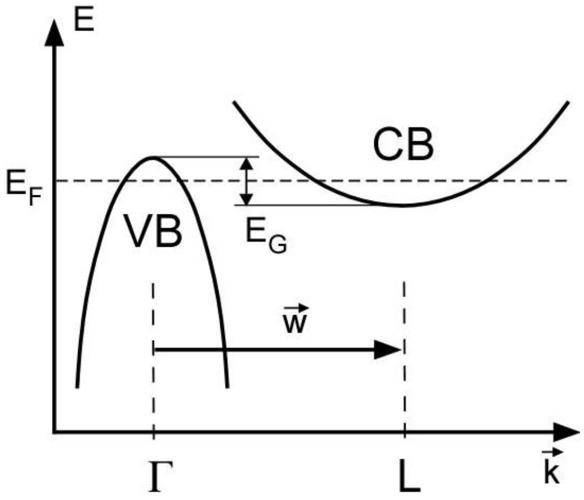
The excitonic insulator: a BCS-like model (mean field)

$$H = H_0 + W$$

$$H_0 = \sum_k \epsilon_a(k) a^+(k) a(k) + \sum_{k,w} \epsilon_b(k,w) b^+(k+w) b(k+w).$$

1-electron Hamiltonian

Valence band
Maximum at Γ



Conduction band
Minima at w

$$W = \sum_{q,w} \rho_a(q) V_c(q) \rho^+_{b,w}(q)$$

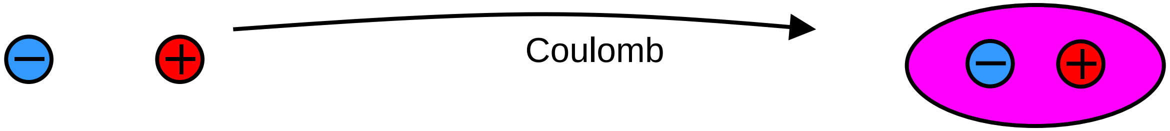
Coulomb
electron-hole interaction

Idea : exciton = electron+hole = boson

COHERENT MACROSCOPIC STATE OF CONDENSED EXCITONS

C.Monney et al, PRB ***79****, 045116 (2009)*

Excitons condensation?



electron + hole

Coulomb

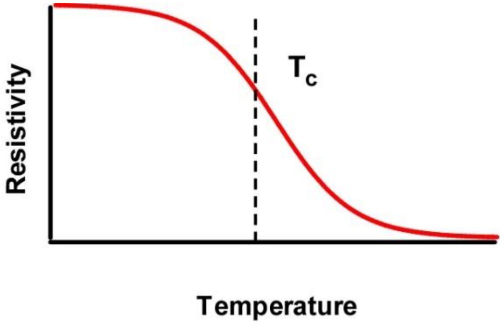
Exciton

charge -e +e

e*=0

→ insulating!

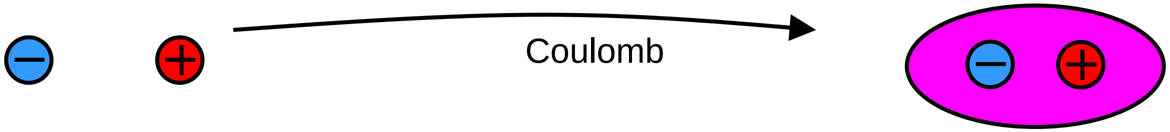
resistivity decreases at LT



Excitons condensation?

electron + hole

Exciton



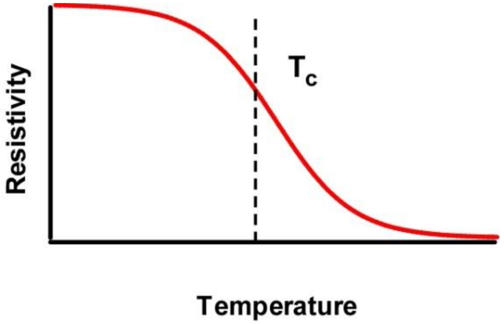
charge

-e

+e

e*=0

→ insulating!



resistivity decreases at LT

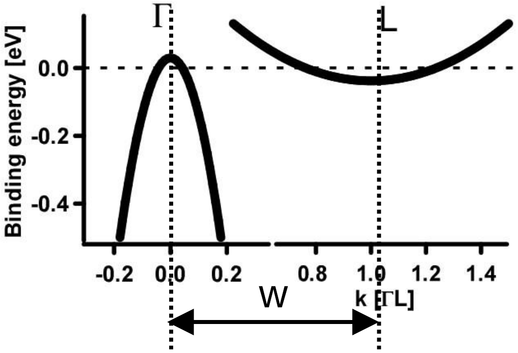
center of mass momentum

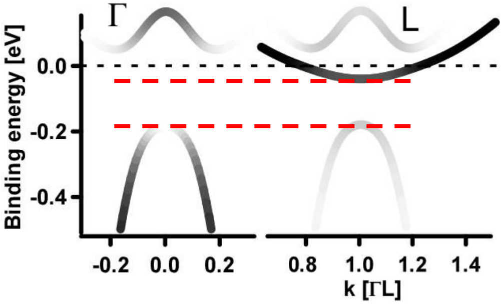
k

k+w

Q ~ w

gap below E_F





CDW of wavevector w

The excitonic insulator: Spectral function

Valence band spectral function (1w):

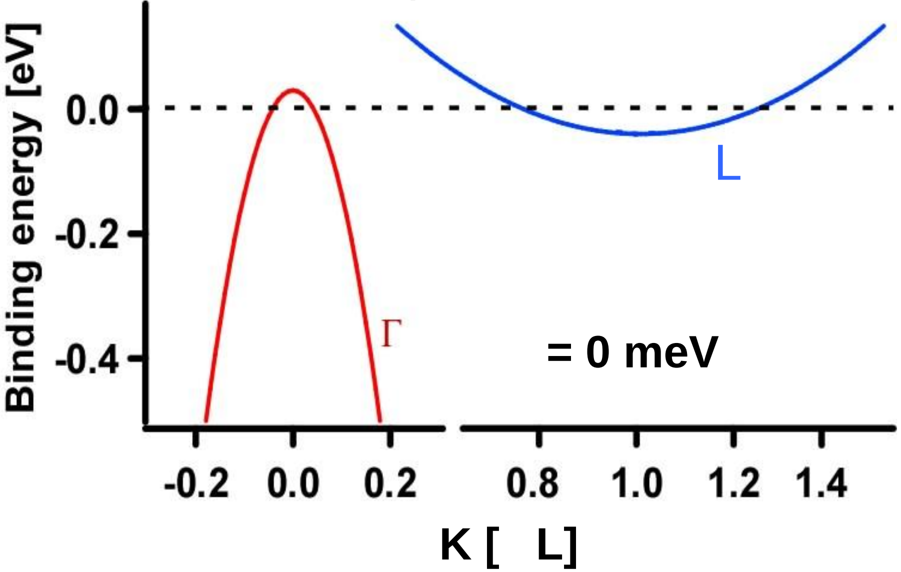
$$A_v(\vec{p},z)=\frac{1}{\pi}\left|\mathrm{Im}\left[G_v(\vec{p},z)\right]\right|=\frac{1}{\pi}\left|\mathrm{Im}\left[\frac{z-\varepsilon_c(\vec{p}+\vec{w})}{(z-\varepsilon_v(\vec{p}))(z-\varepsilon_c(\vec{p}+\vec{w}))-\left|\Delta(\vec{p},\vec{w})\right|^2}\right]\right|$$

to calculate photoemission intensity maps

- -

Calculated band dispersions (3w)

normal phase: **or** L



The excitonic insulator: Spectral function

Valence band spectral function (1w):

Numerator gives the spectral weight

$$A_v(\vec{p},z) = \frac{1}{\pi}\left|\mathrm{Im}\, G_v(\vec{p},z)\right| = \frac{1}{\pi}\left|\mathrm{Im}\left[\frac{z-\varepsilon_c(\vec{p}+\vec{w})}{(z-\varepsilon_v(\vec{p}))(z-\varepsilon_c(\vec{p}+\vec{w}))-\left|\Delta(\vec{p},\vec{w})\right|^2}\right]\right|$$

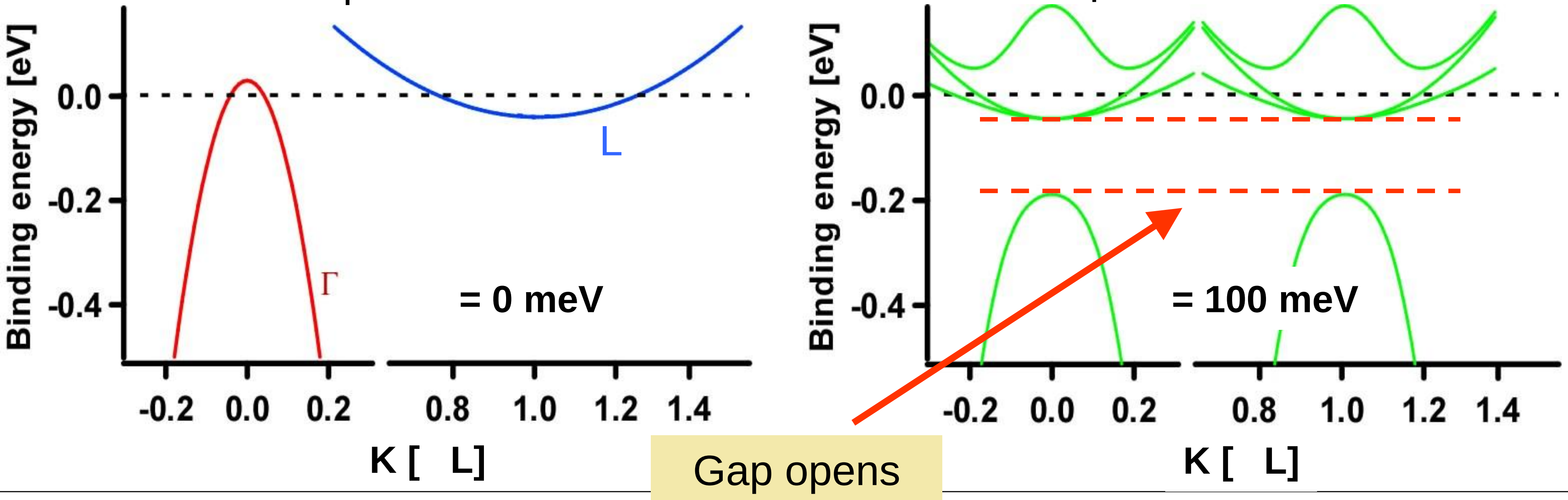
to calculate photoemission intensity maps

Roots of the denominator are the renormalized dispersions

Calculated band dispersions (3w)

normal phase: **or** L

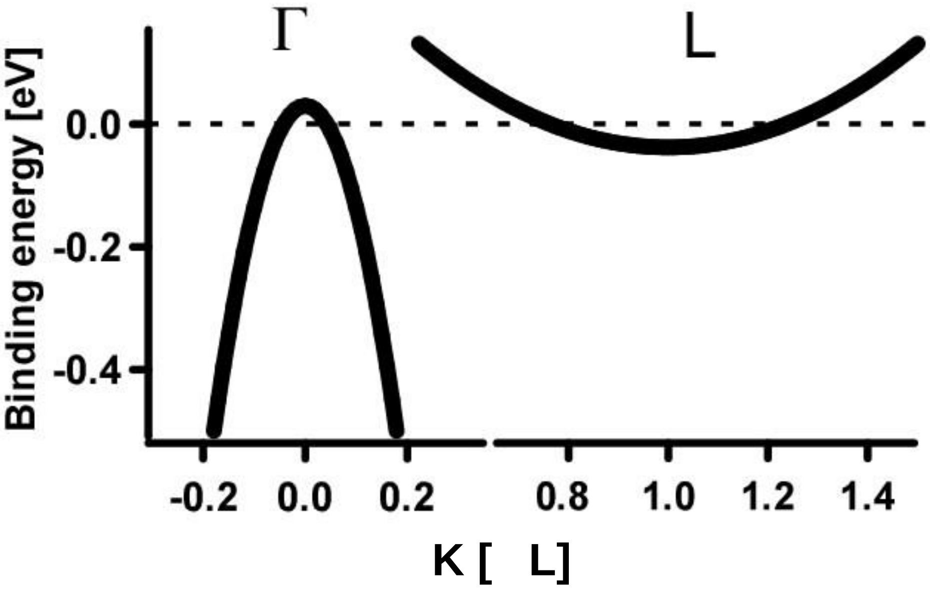
CDW phase: **and** L



Gap opens

The excitonic insulator: Spectral weight

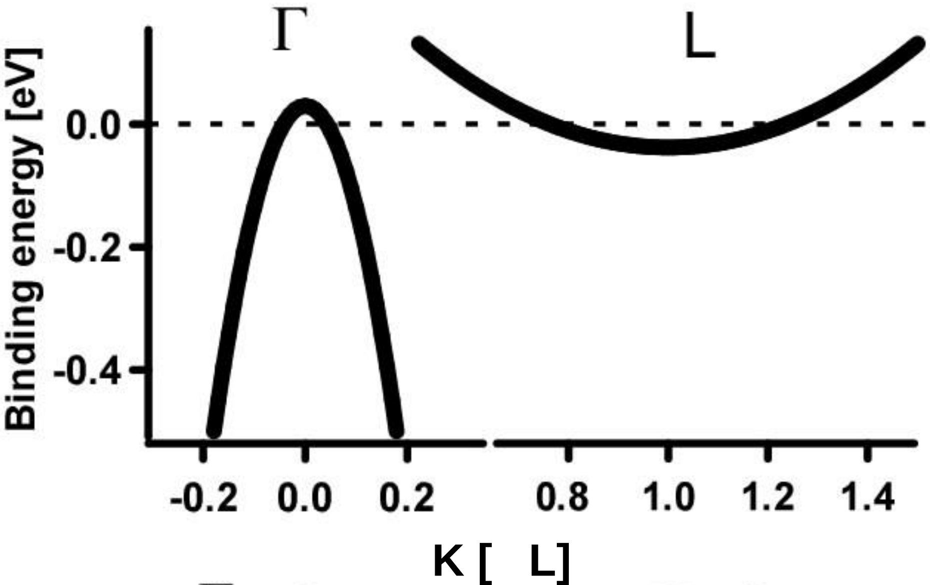
Normal phase
= 0 meV



Large transfer
of spectral
weight
into backfolded
bands

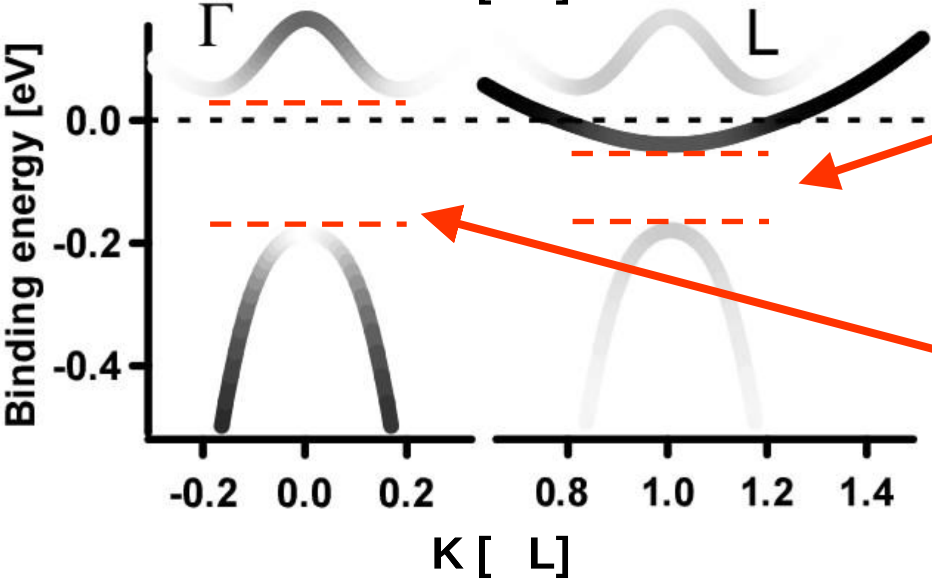
The excitonic insulator: Spectral weight

Normal phase
= 0 meV



Large transfer
of spectral
weight
into backfolded
bands

CDW phase
= 100 meV



Gap opens **below E_F** at L

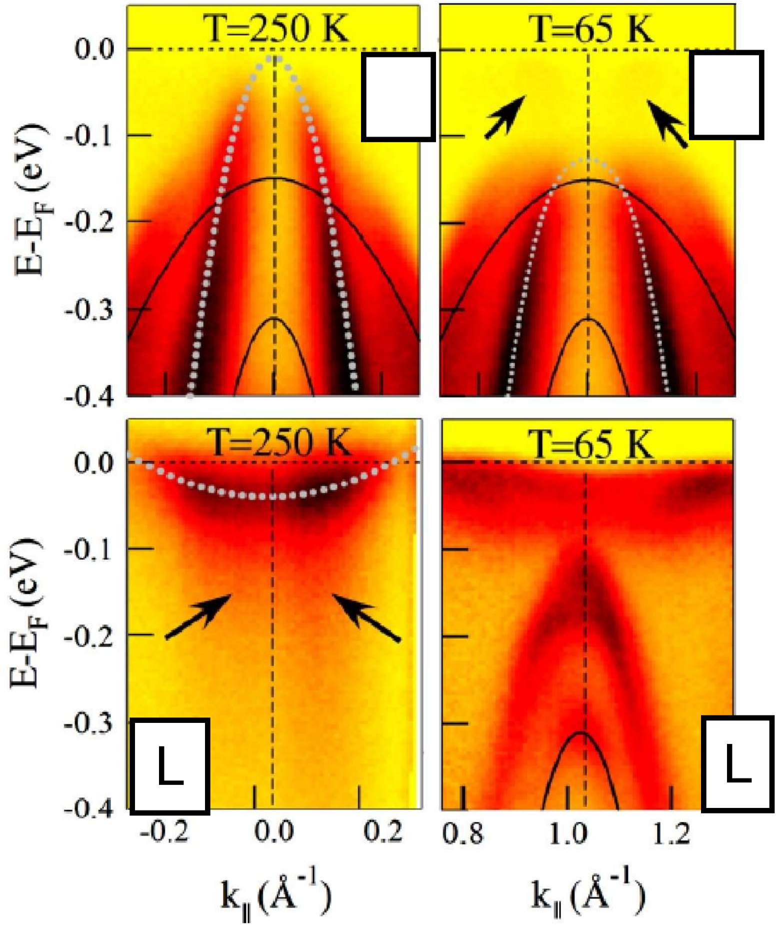
Gap opens **at E_F** at

→ Due to spectral weights and L become inequivalent

Comparison model-experiment

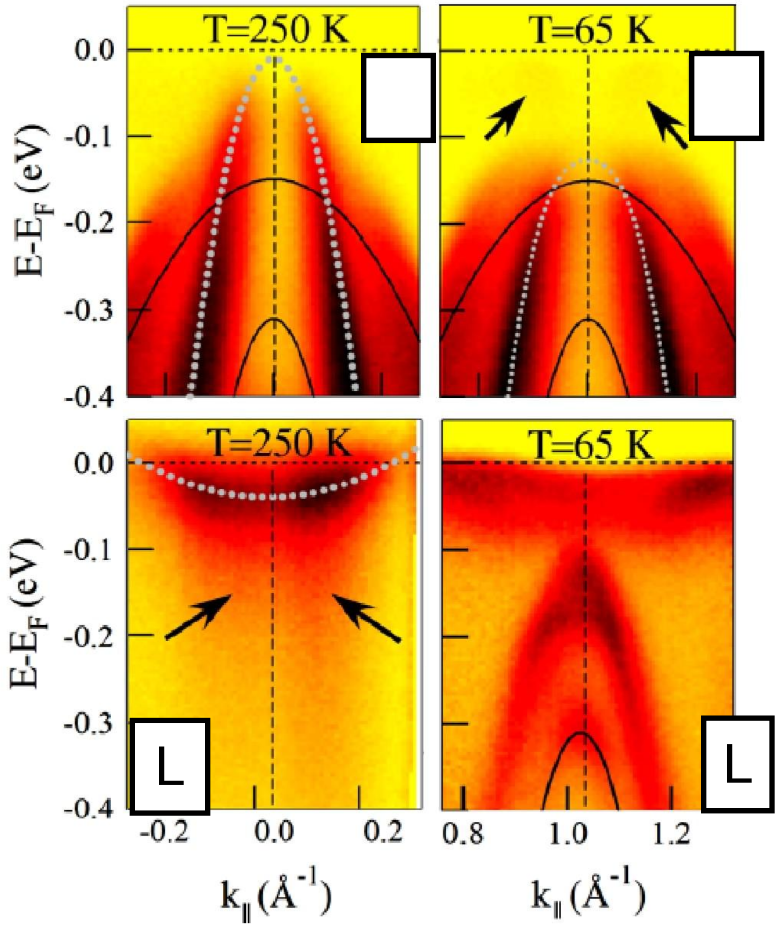
ARPES Experiment

E_G=-70 meV



Comparison model-experiment

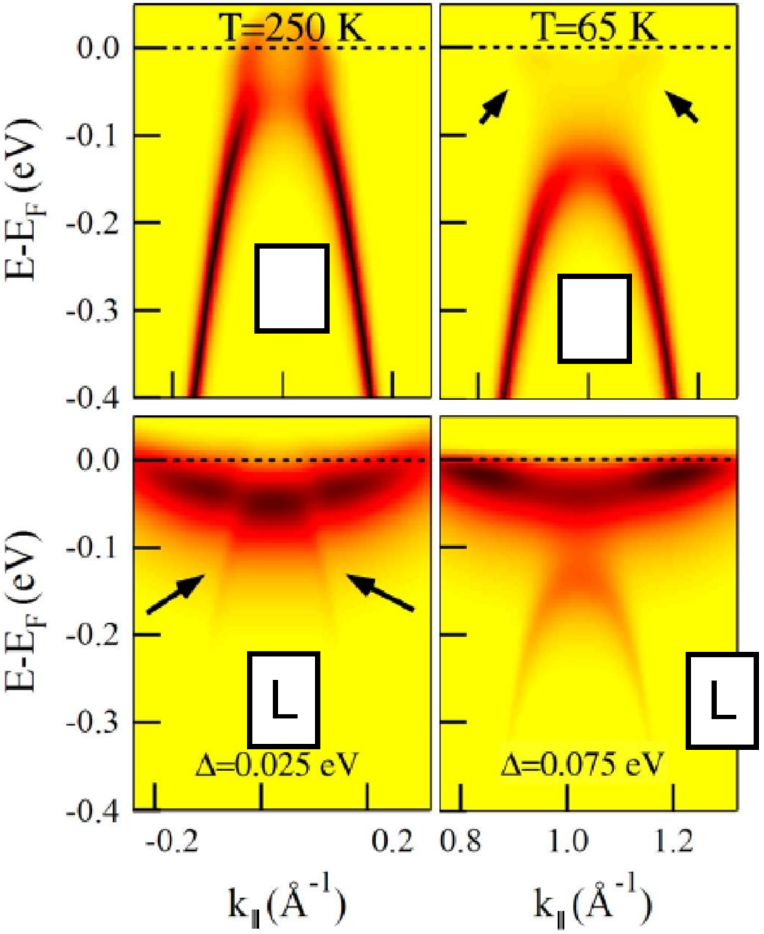
ARPES Experiment



E_G=-70 meV

Model calculation

Δ = 25 meV Δ = 75 meV



→ Large transfer of spectral weight of purely electronic origin

H. Cercellier, C.M. *et al.*, Phys. Rev. Lett. **99**, 146403 (2007)

Comparison model-experiment

ARPES Experiment

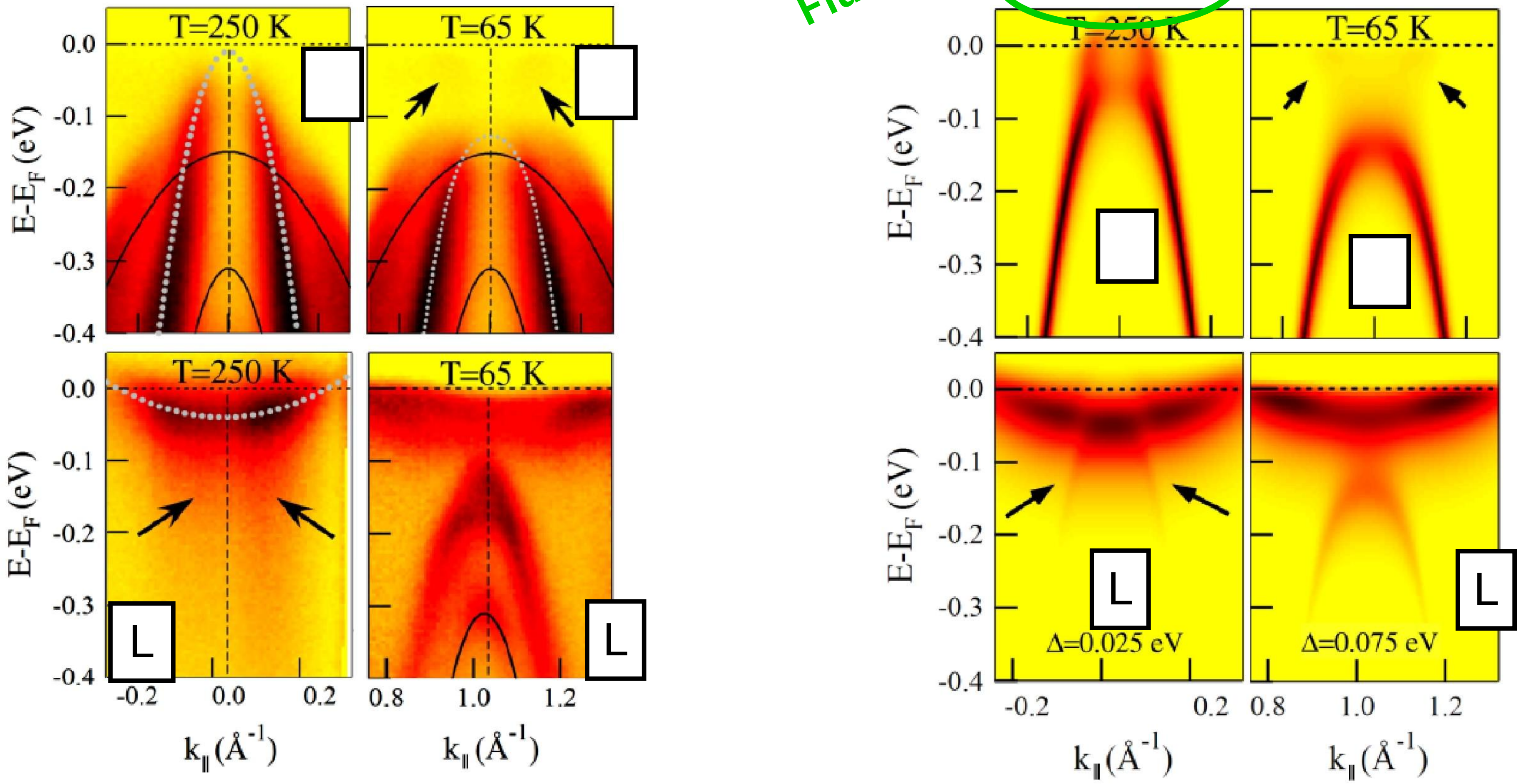
E_G=-70 meV

Fluctuations!

Model calculation

Δ = 25 meV

Δ = 75 meV



→ Large transfer of spectral weight of purely electronic origin

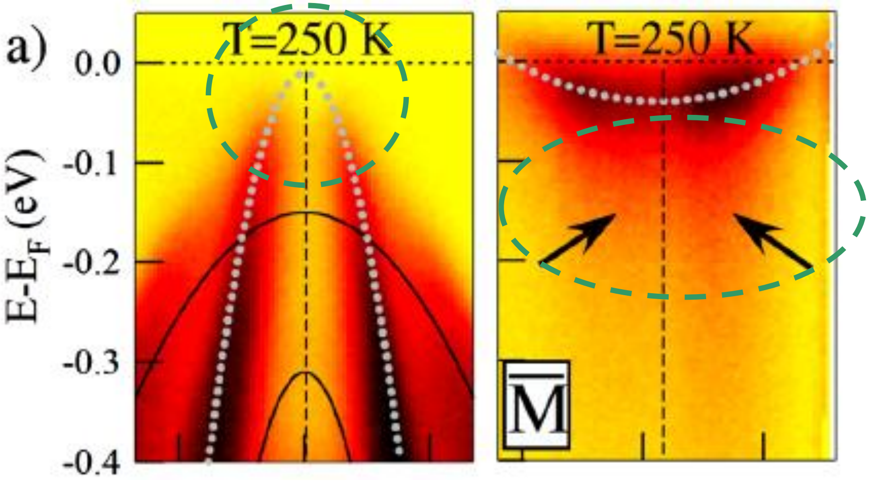
H. Cercellier, C.M. *et al.*, Phys. Rev. Lett. **99**, 146403 (2007)

Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

Hints for electron-hole fluctuations in ARPES

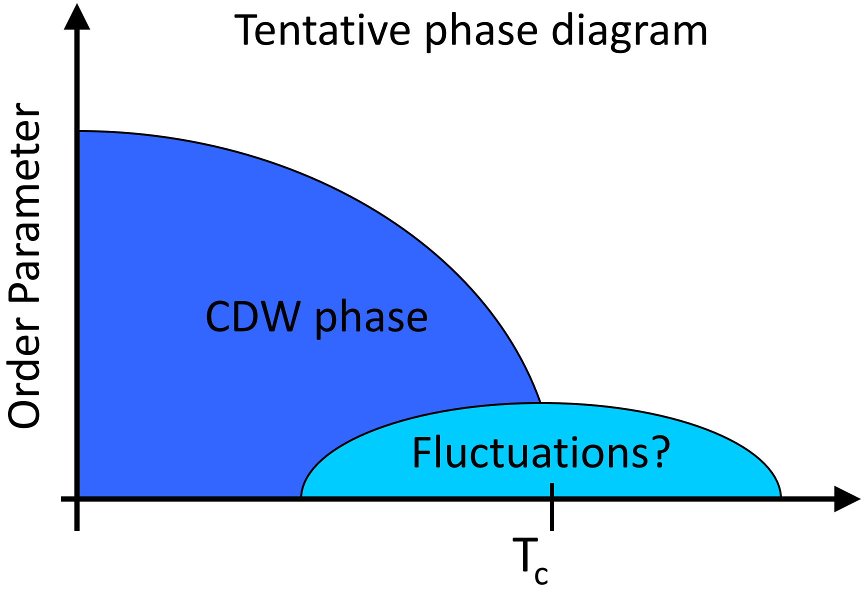
Effects above T_c similar to those below T_c!



This points towards strong fluctuations in this quasi-2D system!

What is the nature of these fluctuations (above T_c)?

Do they tell us something about the origin of the CDW transition?



Correction to the bare dispersions: self-energy

« 1st » order perturbation theory to tackle fluctuations (above T_c):

$$G^{(0)}(\vec{k},z) = \frac{1}{z-\varepsilon(\vec{k})} \longrightarrow G(\vec{k},z) = \frac{1}{z-\varepsilon(\vec{k}) - \boxed{\sigma(\vec{k},z)}}$$

The self-energy (k,z) encapsulates the many-body corrections due to electron-hole interactions.

Correction to the bare dispersions: self-energy

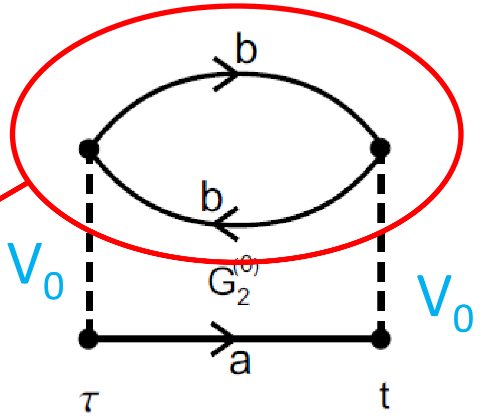
« 1st » order perturbation theory to tackle fluctuations (above T_c):

$$G^{(0)}(\vec{k},z) = \frac{1}{z-\varepsilon(\vec{k})} \longrightarrow G(\vec{k},z) = \frac{1}{z-\varepsilon(\vec{k}) - \boxed{\sigma(\vec{k},z)}}$$

The self-energy (k,z) encapsulates the many-body corrections due to electron-hole interactions.

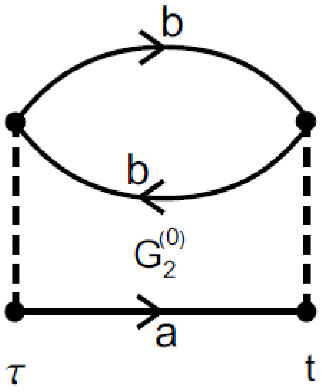
We focus on the Coulomb interaction between holes (valence band) and electrons (conduction band).

We have calculated this type of diagram (polarization bubble):



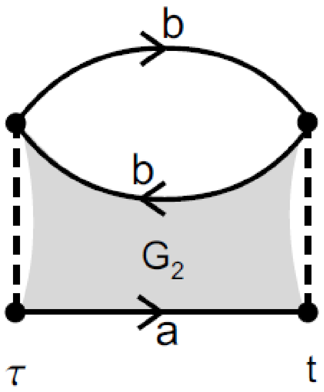
electron-hole pairs renormalizing the GF

Electron-hole correlations in the self energy

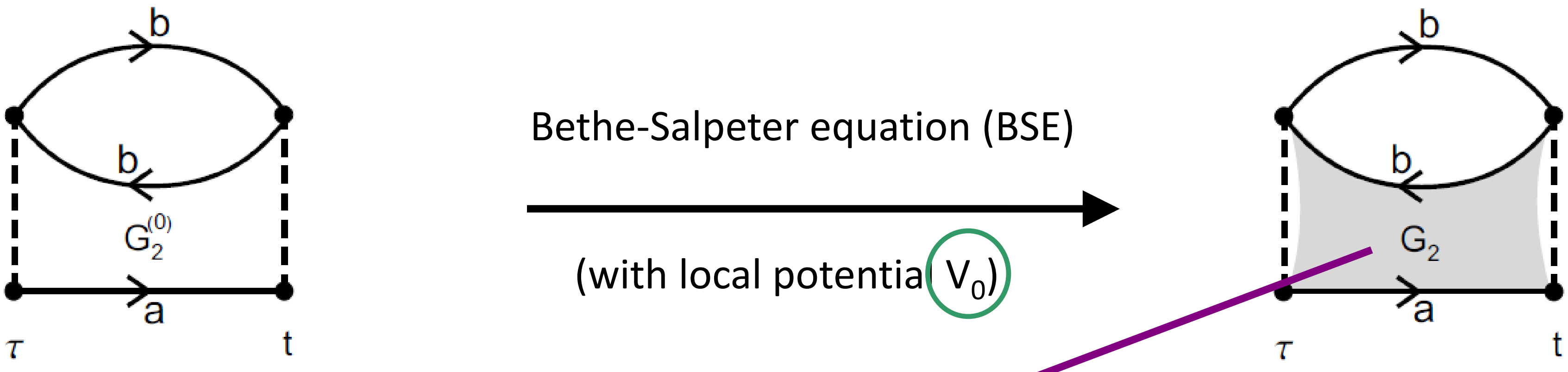


Bethe-Salpeter equation (BSE)

(with local potential V_0)



Electron-hole correlations in the self energy



Bethe-Salpeter equation (BSE)

(with local potential V_0)

We use the function:

$$X_i(\vec{Q},z) = \int d^3p\, d^3p'\, \underline{G_2^i(\vec{Q},\vec{p},\vec{p}\,',z)}$$

( )

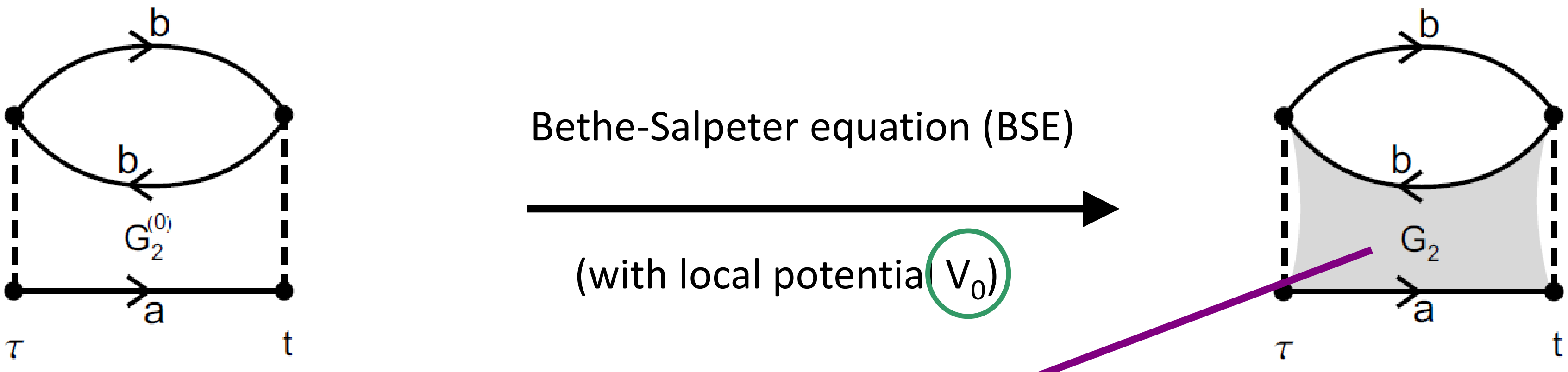
related to the electronic susceptibility

which obeys to (due to BSE):

$$X_i(\vec{Q},z) \propto \frac{X_i^{(0)}(\vec{Q},z)}{1-\frac{V_0}{(2\pi)^3}X_i^{(0)}(\vec{Q},z)}$$

T-Matrix approach, Bronold and Fehske, PRB **74**, 165107 (2006)

Electron-hole correlations in the self energy



Bethe-Salpeter equation (BSE)

(with local potential V_0)

We use the function:

$$\boxed{X_i(\vec{Q},z)} = \int d^3p\, d^3p'\, \underline{G_2^i(\vec{Q},\vec{p},\vec{p}\,',z)}$$

( )

related to the electronic susceptibility

which obeys to (due to BSE):

$$X_i(\vec{Q},z) \propto \frac{X_i^{(0)}(\vec{Q},z)}{1-\frac{V_0}{(2\pi)^3}X_i^{(0)}(\vec{Q},z)}\Bigg\}\longrightarrow$$

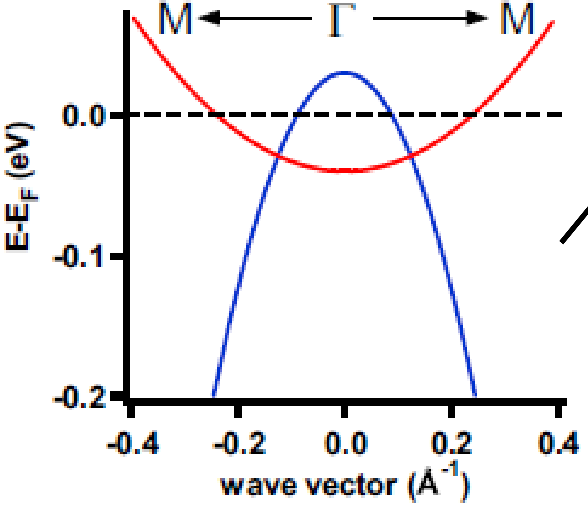
...=0 for

-> instability of system due to e-h interactions!

T-Matrix approach, Bronold and Fehske, PRB **74**, 165107 (2006)

Fermiology: is nesting important?

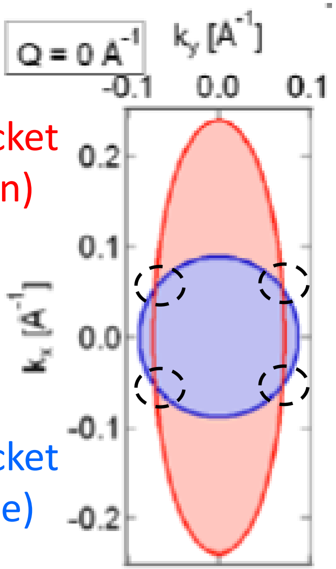
2-band system
semimetal

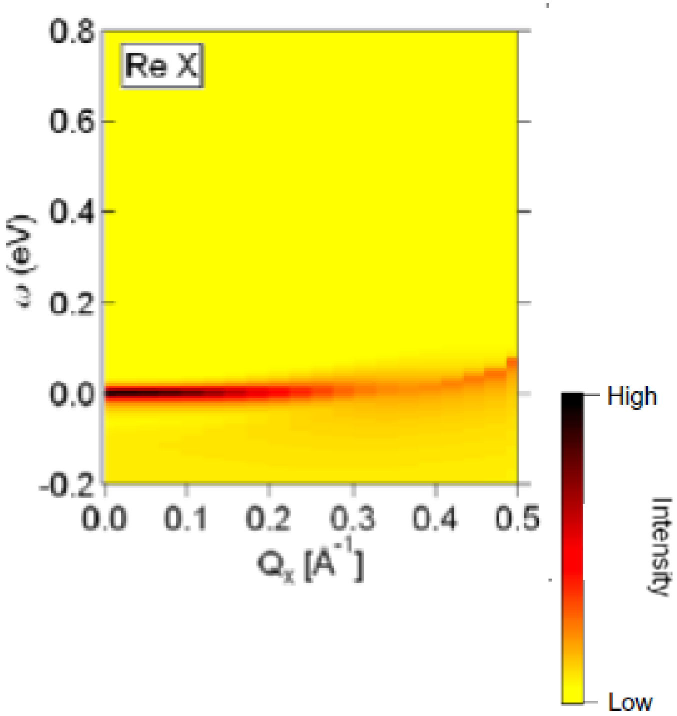


?

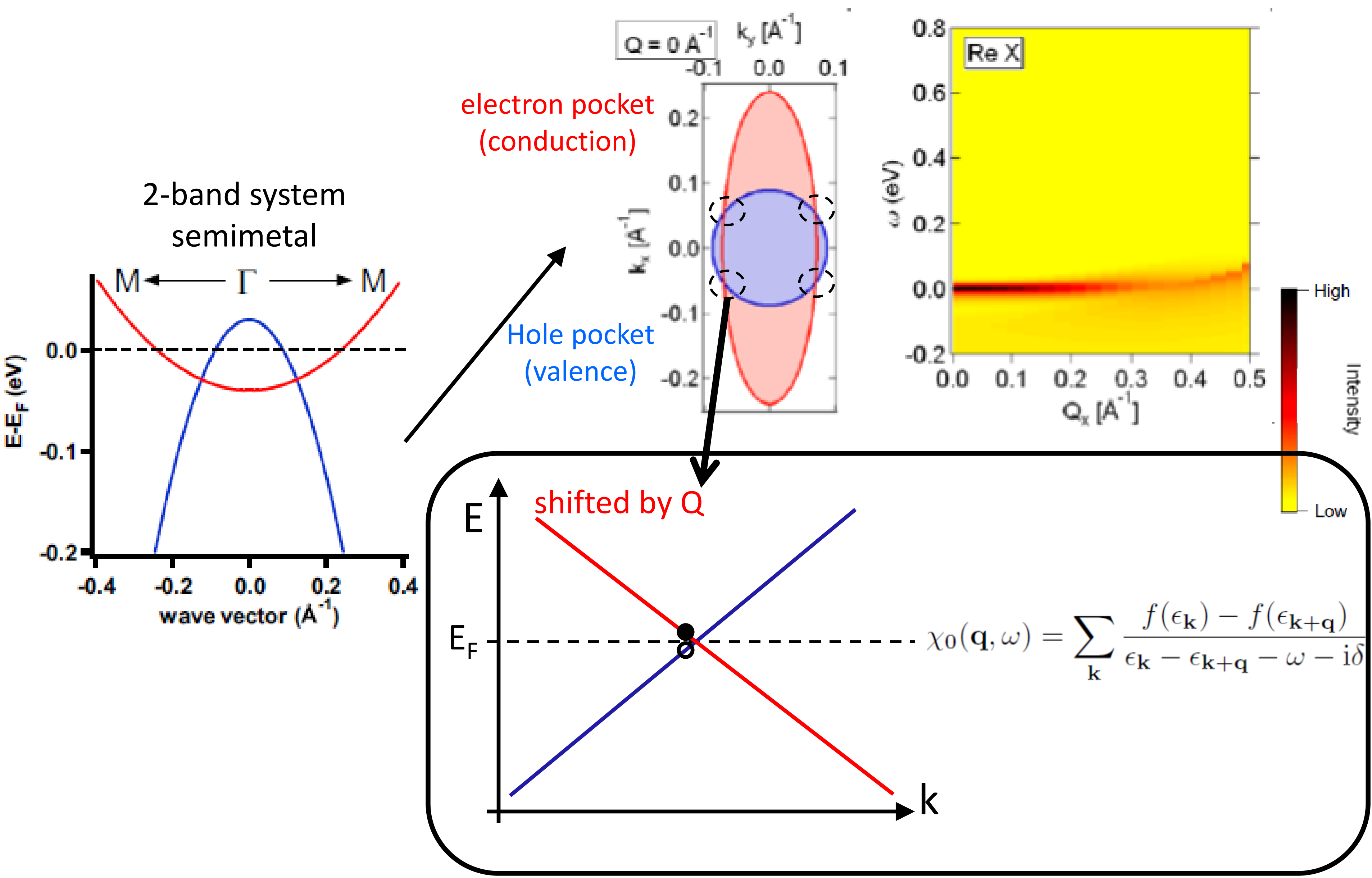
electron pocket
(conduction)

Hole pocket
(valence)





Fermiology: is nesting important?



2-band system
semimetal

electron pocket
(conduction)

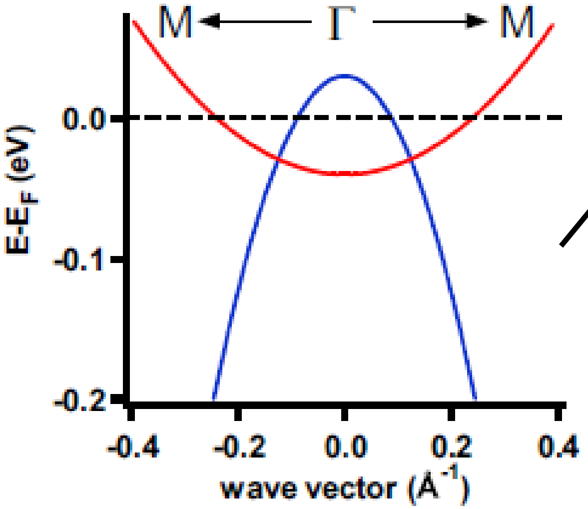
Hole pocket
(valence)

shifted by Q

$$\chi_0(\mathbf{q},\omega) = \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \omega - i\delta}$$

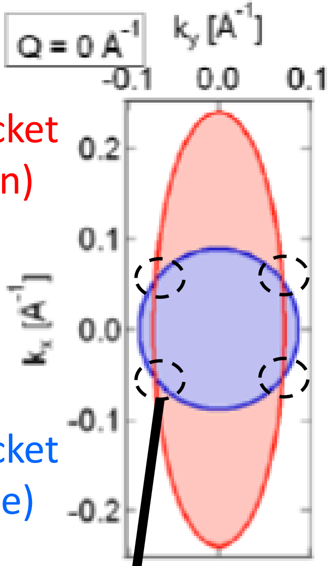
Fermiology: is nesting important?

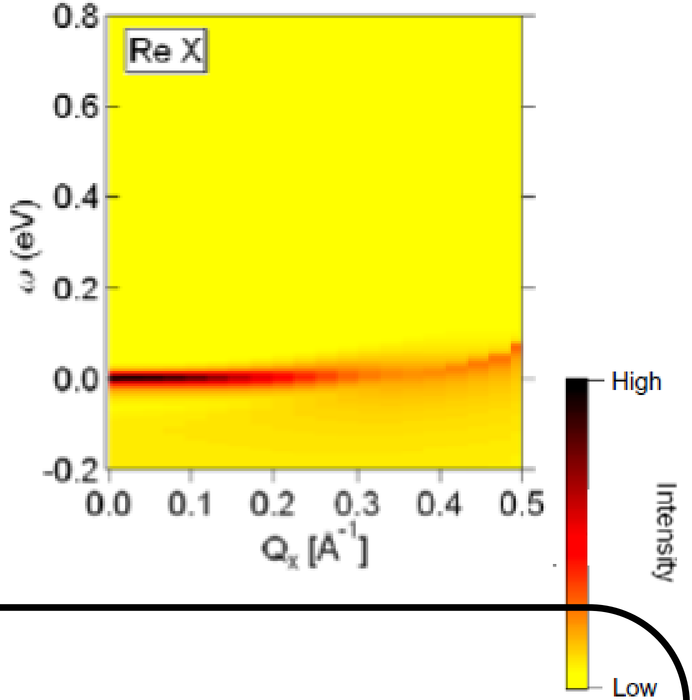
2-band system
semimetal

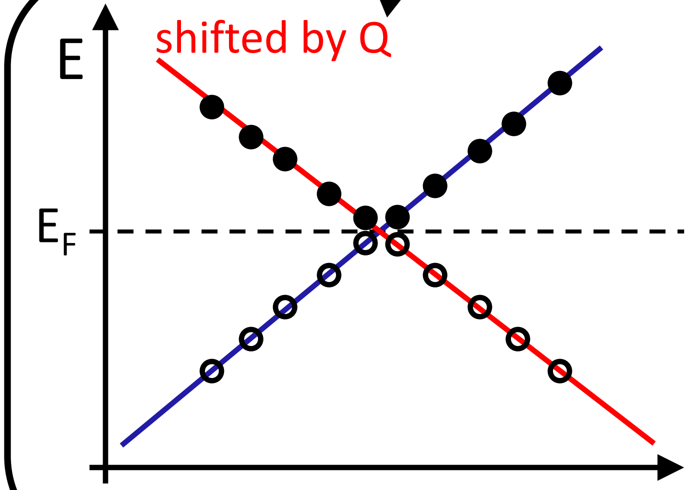


electron pocket
(conduction)

Hole pocket
(valence)







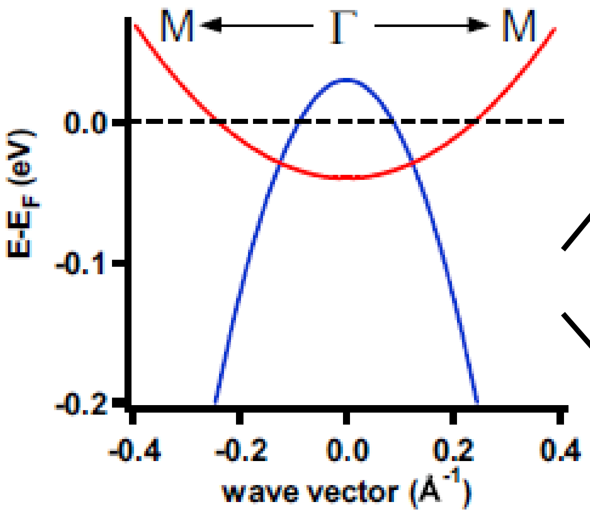
shifted by Q

$$\chi_0(\mathbf{q},\omega) = \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \omega - i\delta}$$

interband transition for a whole energy range!

Fermiology: is nesting important?

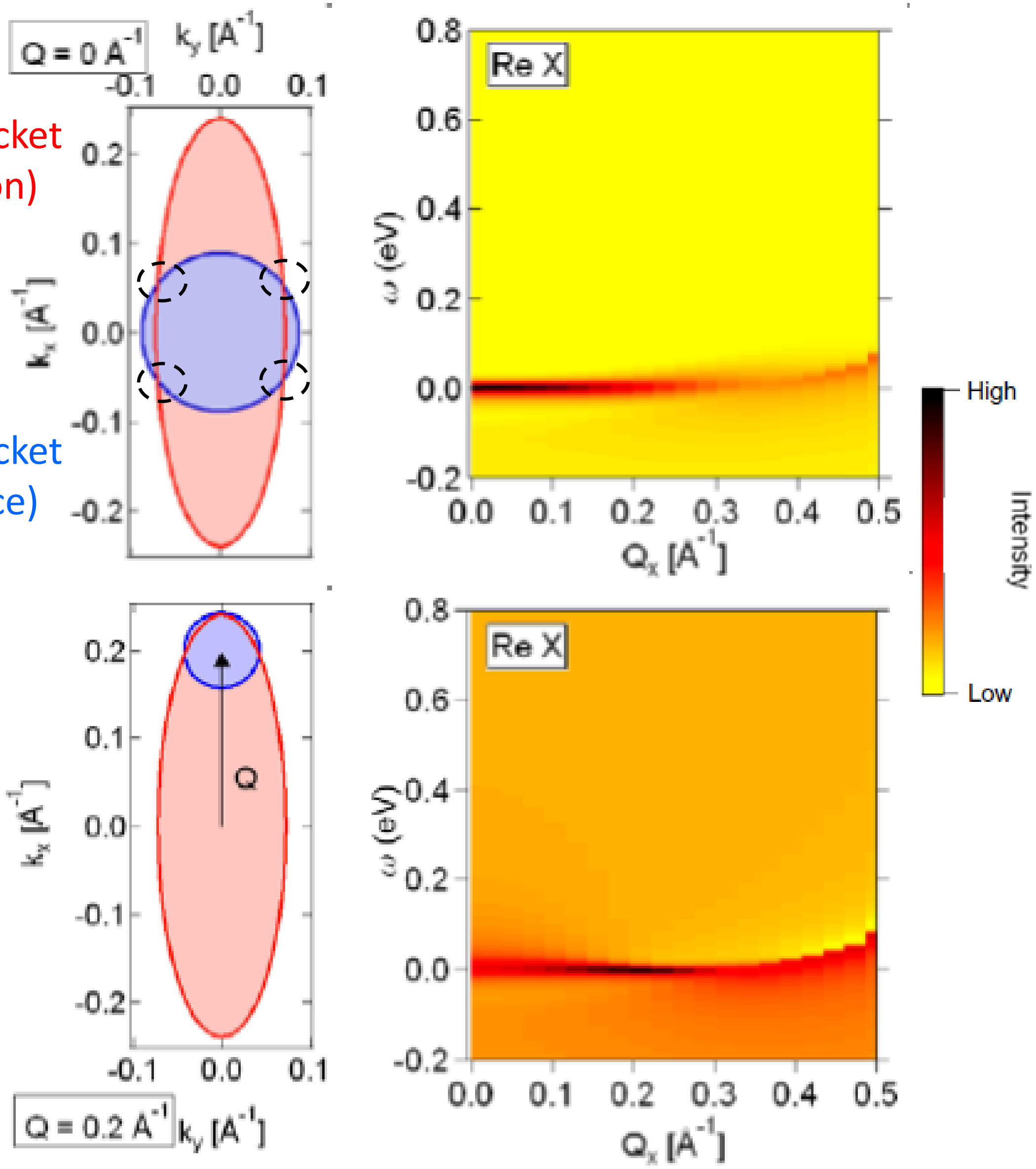
2-band system
semimetal



electron pocket
(conduction)

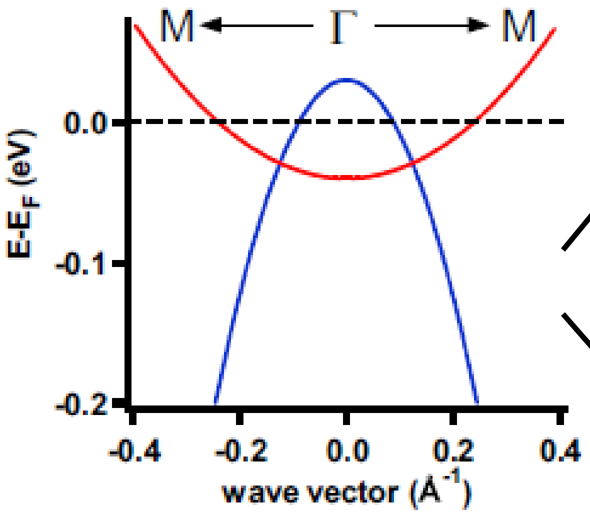
Hole pocket
(valence)

?



Fermiology: is nesting important?

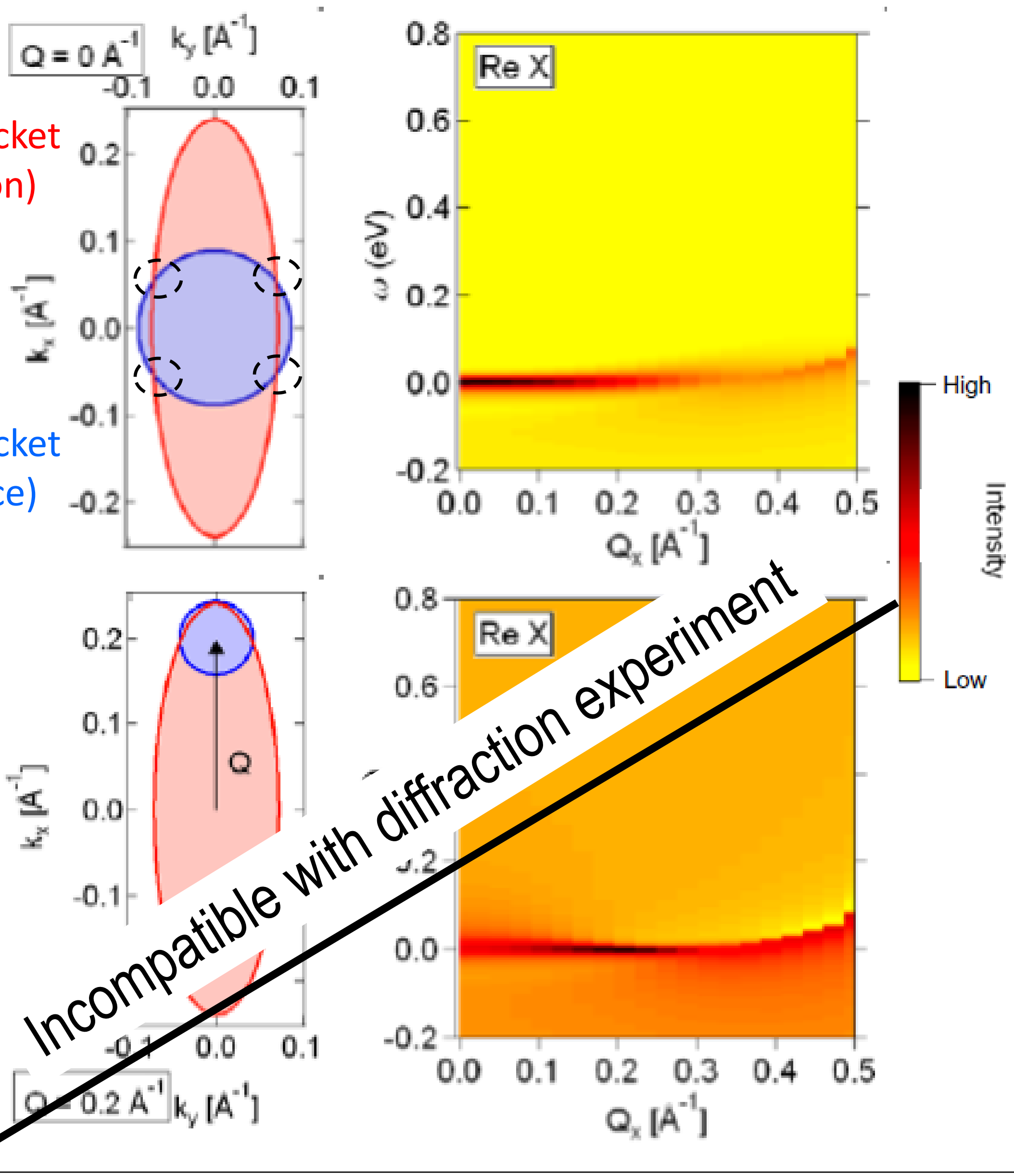
2-band system
semimetal



?

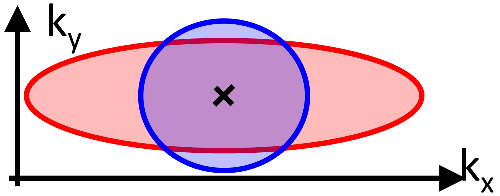
electron pocket
(conduction)

Hole pocket
(valence)



Incompatible with diffraction experiment

Electron-hole driven instability



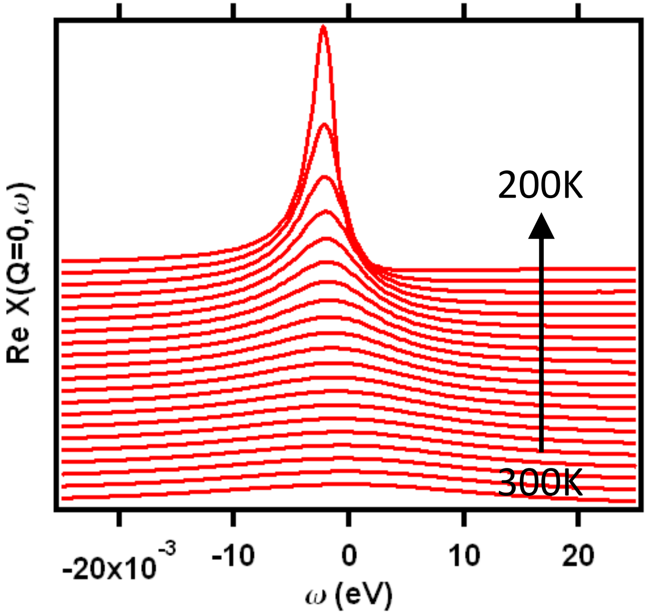
2-band system

$$X_i(\vec{Q},z) \propto \frac{X_i^{(0)}(\vec{Q},z)}{\boxed{1-\frac{V_0}{(2\pi)^3}X_i^{(0)}(\vec{Q},z)}}$$

~ electronic susceptibility

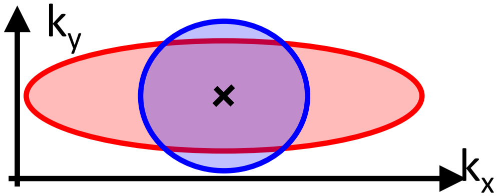
⚠

electronic instability



V_0 chosen such that T_c=200K

Electron-hole driven instability



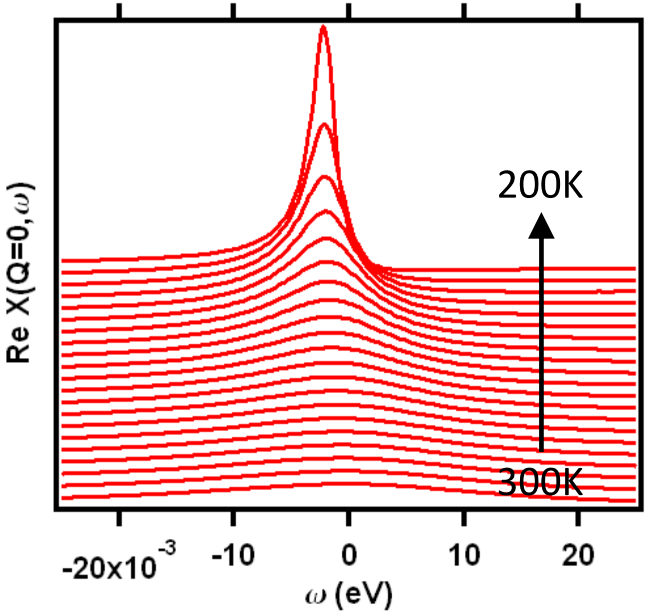
2-band system

$$X_i(\vec{Q},z) \propto \frac{X_i^{(0)}(\vec{Q},z)}{\boxed{1-\frac{V_0}{(2\pi)^3}X_i^{(0)}(\vec{Q},z)}}$$

~ electronic susceptibility

!

electronic instability



V_0 chosen such that T_c=200K

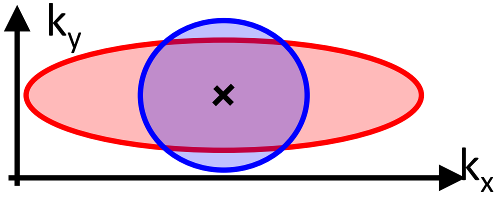
Now calculate self-energy for photoemission:

$$\sigma_a(\vec{p},z_\alpha) = V_0^2 \sum_{\vec{Q},i} \int \frac{d\omega}{2\pi} \mathcal{X}_{X_i}(\vec{Q},\omega) \frac{N_B(\omega)+N_F(\varepsilon_{b_i}(\vec{p}+\vec{Q}))}{z_\alpha+\omega-\varepsilon_{b_i}(\vec{p}+\vec{Q})}$$

VB

CB

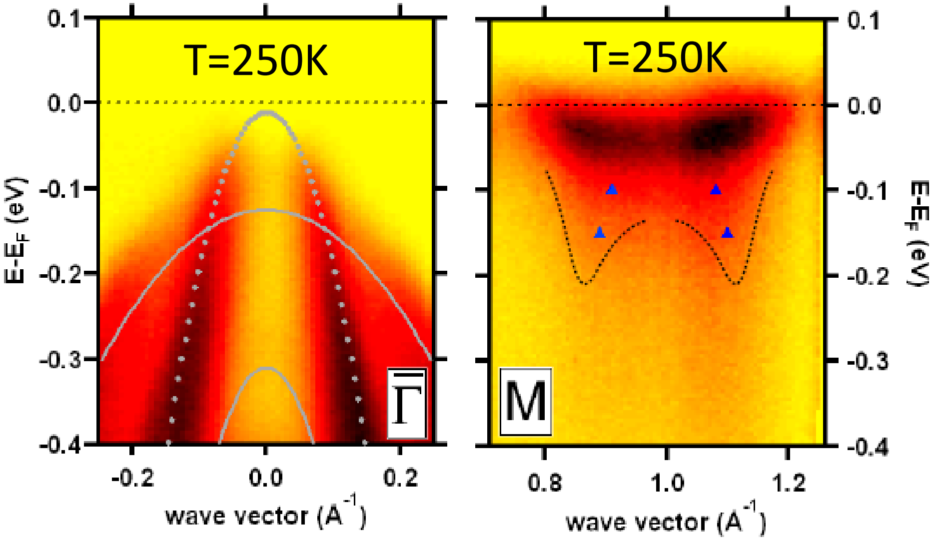
Effect of fluctuations on photoemission



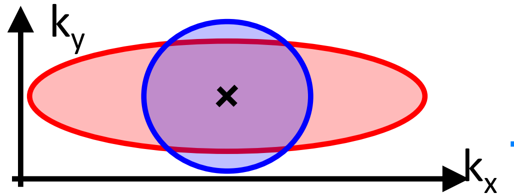
2-band system

Photoemission is proportional to the spectral function:

$$A(\vec{k},\omega) = -\frac{1}{\pi}\mathrm{Im}\, G_{\mathrm{ret}}(\vec{k},\omega) = -\frac{1}{\pi}\frac{\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)}{[\omega-\varepsilon(\vec{k})-\mathrm{Re}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2+[\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2}$$



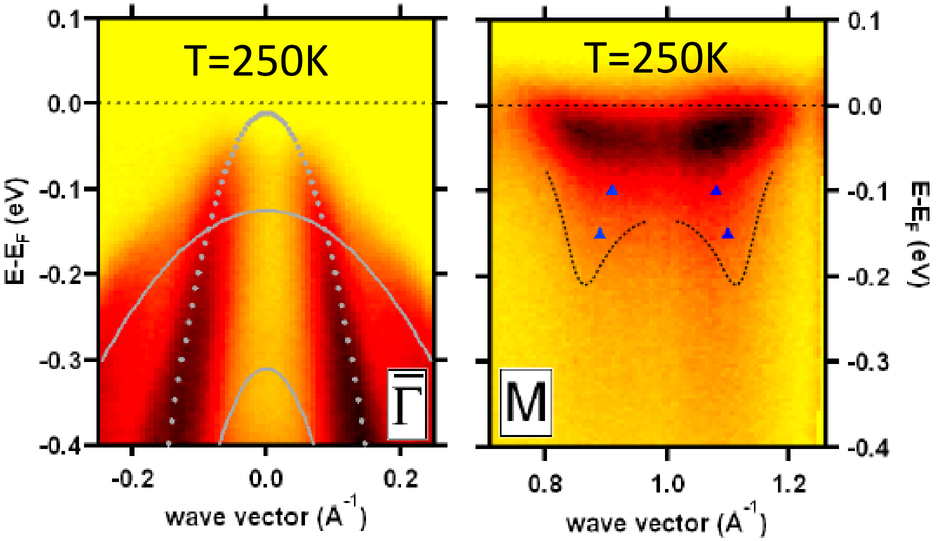
Effect of fluctuations on photoemission

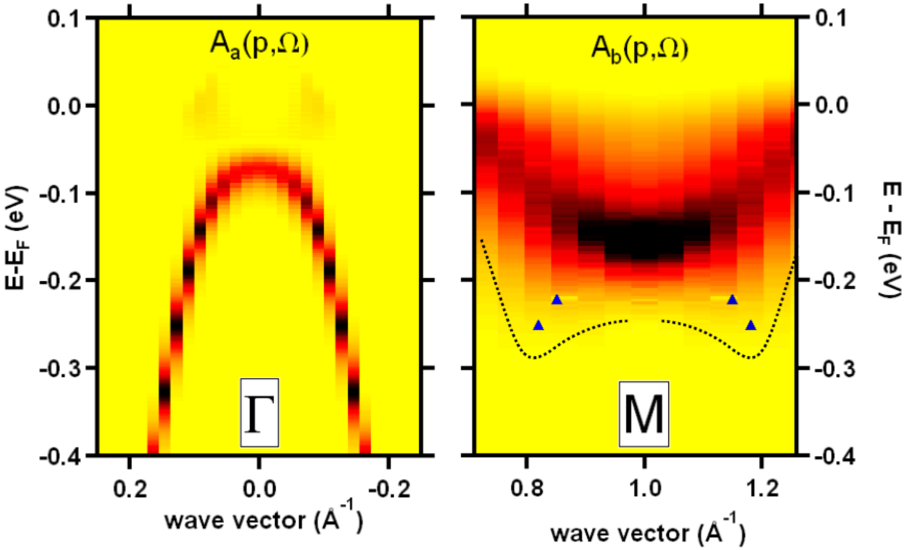


2-band system

Photoemission is proportional to the spectral function:

$$A(\vec{k},\omega) = -\frac{1}{\pi}\mathrm{Im}\, G_{\mathrm{ret}}(\vec{k},\omega) = -\frac{1}{\pi}\frac{\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)}{[\omega - \varepsilon(\vec{k}) - \mathrm{Re}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2 + [\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2}$$

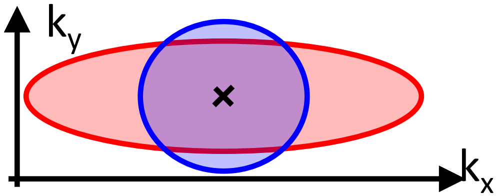




→ Basic effects in the experimental data are understood in the simulation, though weaker.

Too big shift of conduction band can be compensated by chemical potential shift.

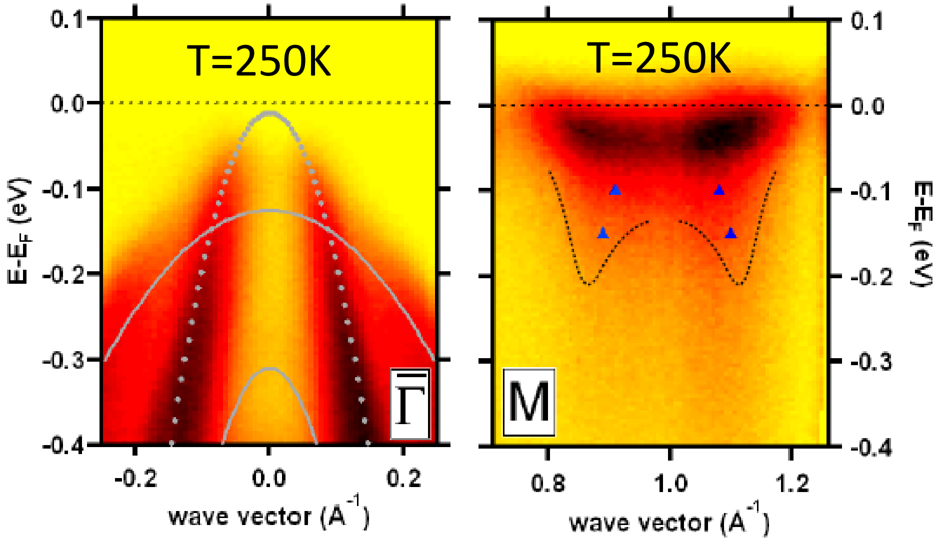
Effect of fluctuations on photoemission

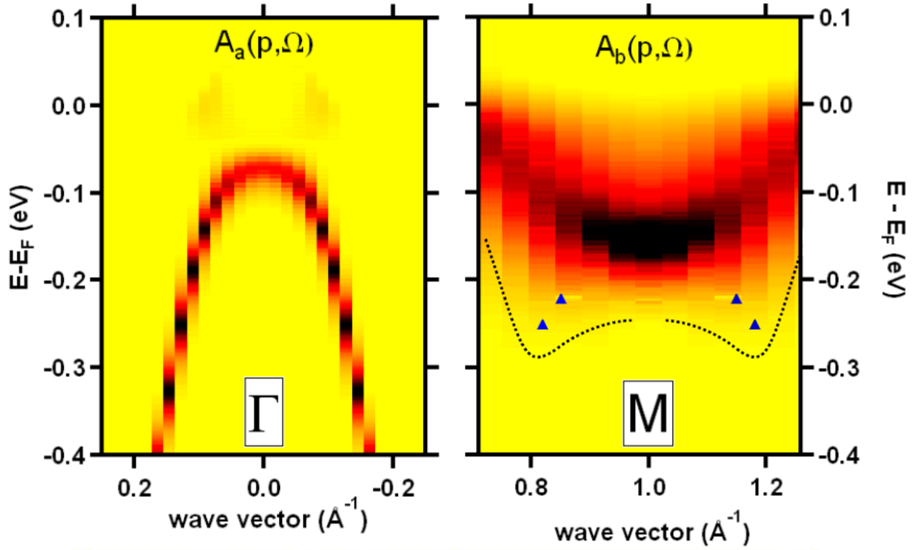


2-band system

Photoemission is proportional to the spectral function:

$$A(\vec{k},\omega) = -\frac{1}{\pi}\mathrm{Im}\, G_{\mathrm{ret}}(\vec{k},\omega) = -\frac{1}{\pi}\frac{\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)}{[\omega-\varepsilon(\vec{k})-\mathrm{Re}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2+[\mathrm{Im}\,\sigma_{\mathrm{ret}}(\vec{k},\omega)]^2}$$

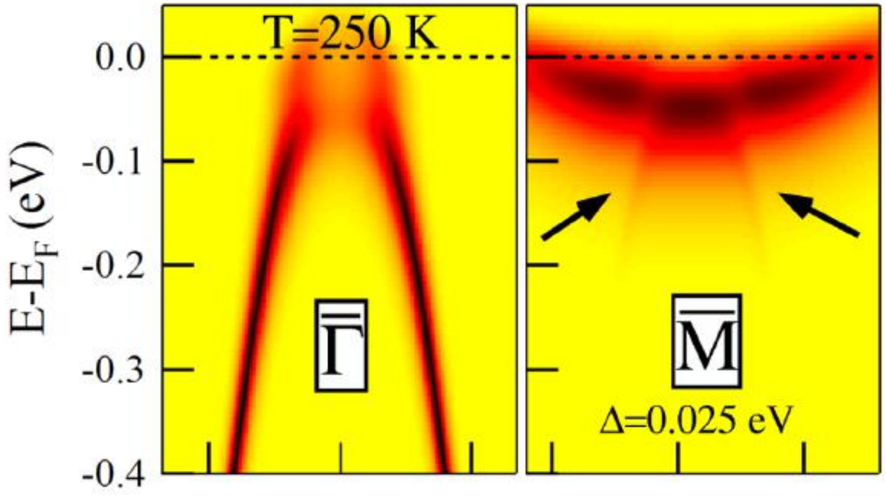




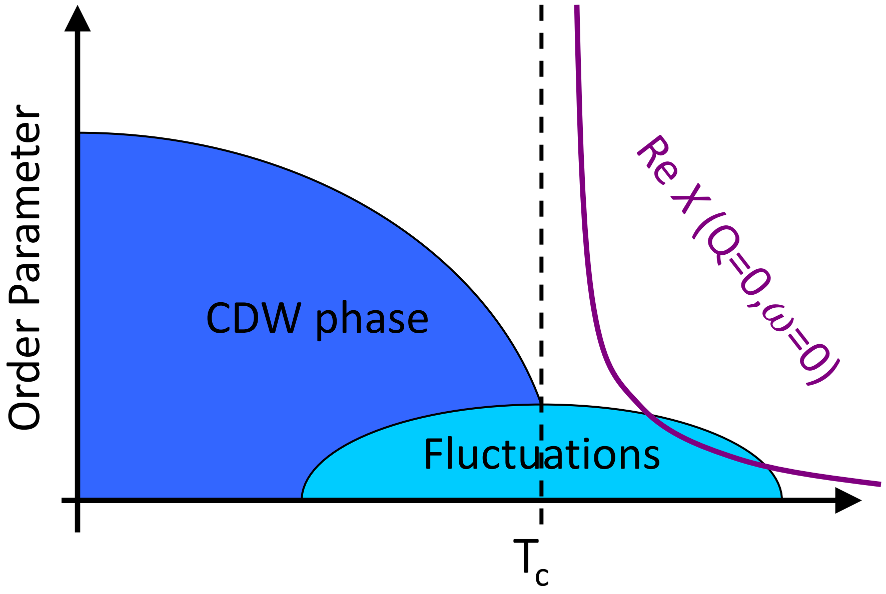
→ E-h fluctuation effects on bands anticipate the effect of the exciton condensate!

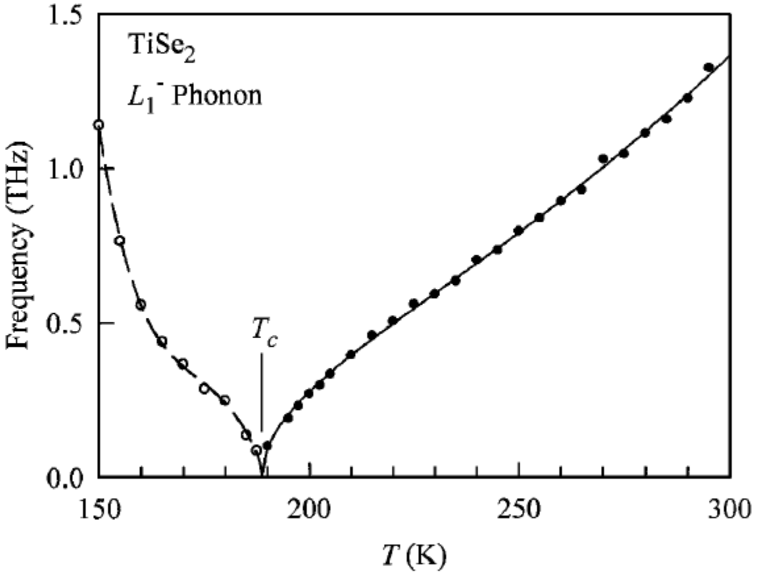
Kind of pseudo-gap phase.

C.M. *et al.*, PRB **85**, 235150 (2012)



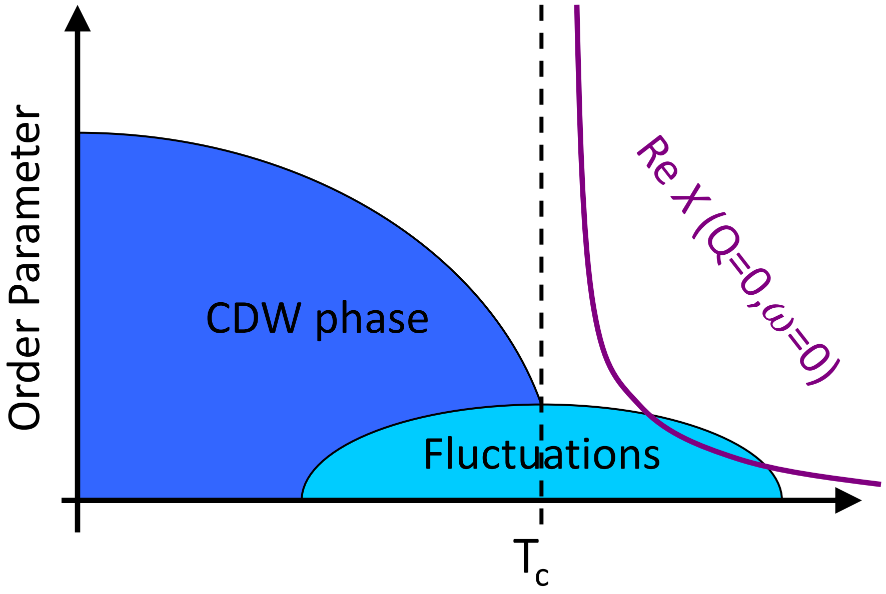
Effect of the electronic instability on the lattice

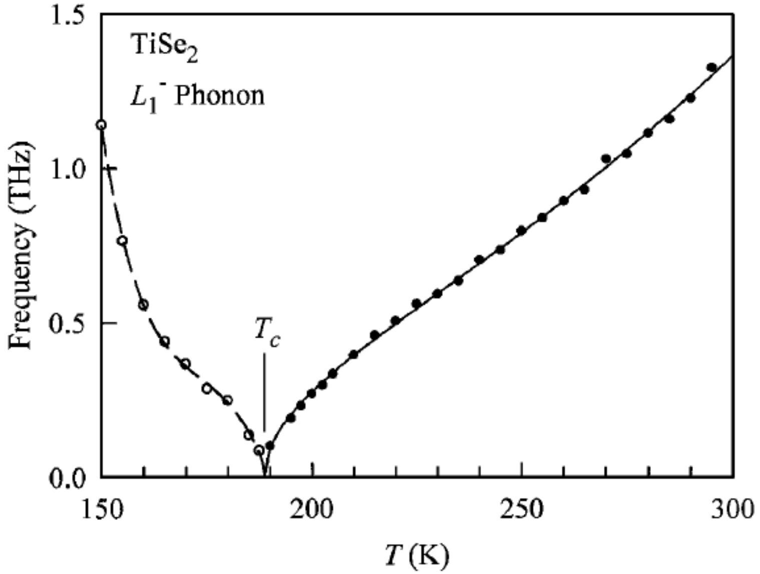




Holt *et al.*, PRL **86**, 3799 (2001)

Effect of the electronic instability on the lattice





Holt *et al.*, PRL **86**, 3799 (2001)

electron-phonon coupling

$$\Omega^2 = \omega^2 + \mathrm{Re}\,\sigma_{\mathrm{ph}}(\vec{Q}=0,\Omega) = \omega^2 - \frac{g^2}{4}\mathrm{Re}\,X(\vec{Q}=0,\Omega)$$

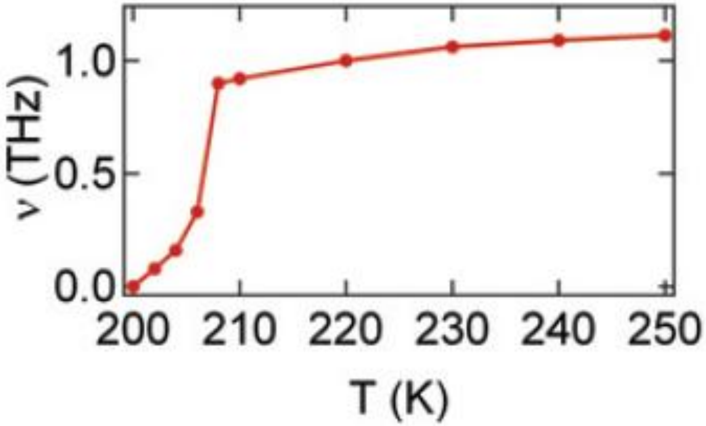
→ Electron-hole instability drives the phonon softening at L

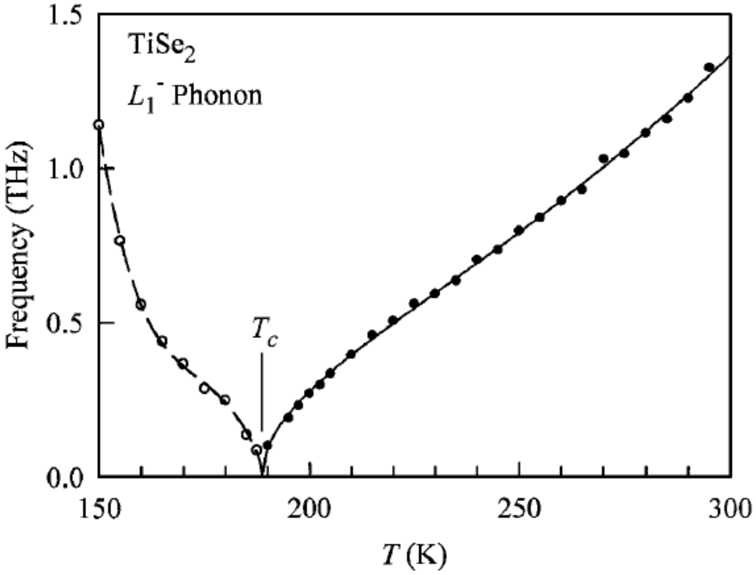
Lattice distortion when = 0

Effect of the electronic instability on the lattice

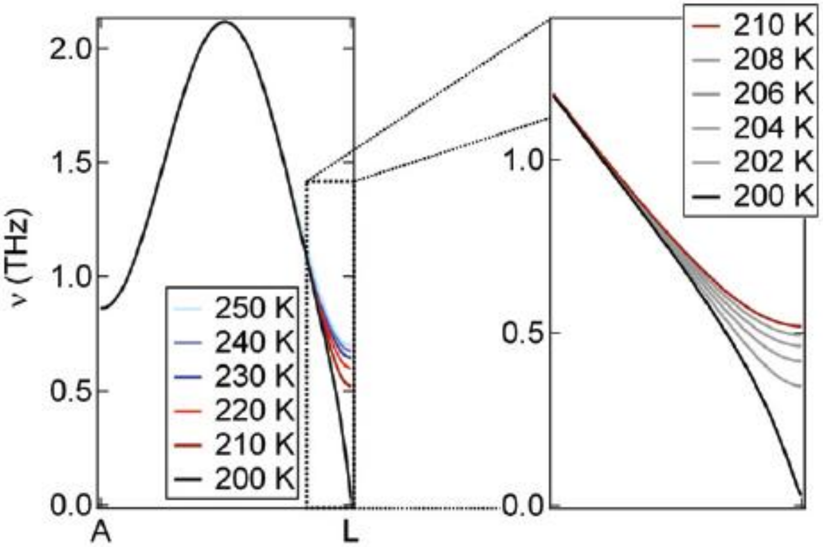
$$\Omega^2 = \omega^2 + \mathrm{Re}\,\sigma_{\mathrm{ph}}(\vec{Q}=0,\Omega) = \omega^2 - \frac{g^2}{4}\mathrm{Re}\,X(\vec{Q}=0,\Omega)$$

$$g = 1.1 \times 10^{12}\,\mathrm{eV}\,\text{Å}^{-1}\,\mathrm{kg}^{-1/2} \qquad \omega_0 = 2\pi \times 1.3\,\mathrm{THz}$$





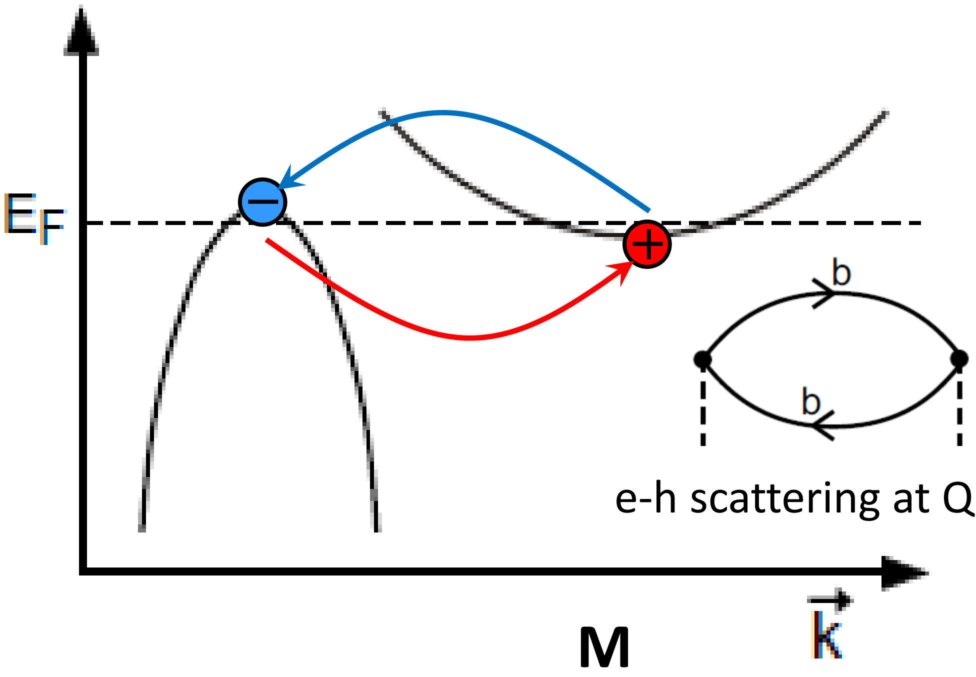
Holt *et al.*, PRL **86**, 3799 (2001)



Calculated e-h self-energy explains the softening of the L-phonon mode for reasonable parameters.

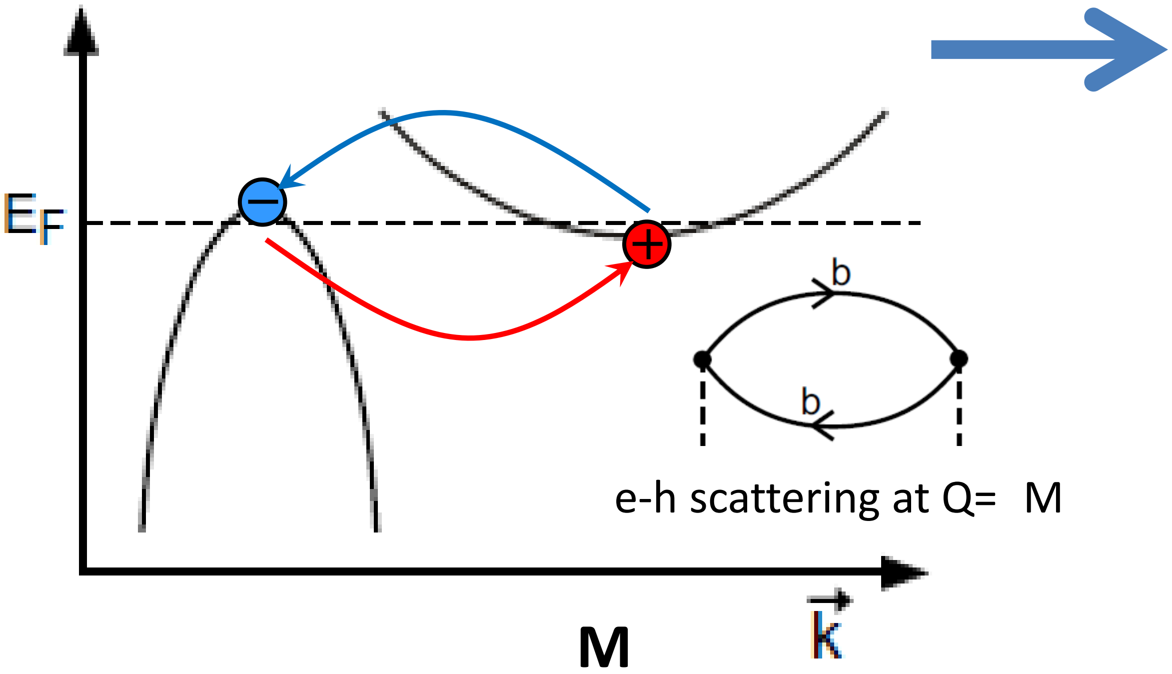
C.M. *et al.*, NJP **14**, 075026 (2012)

From electron-hole fluctuations to the CDW phase

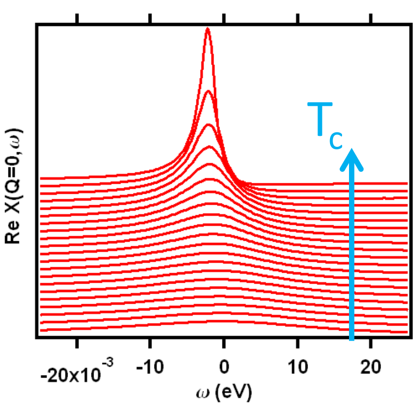


e-h scattering at Q= M

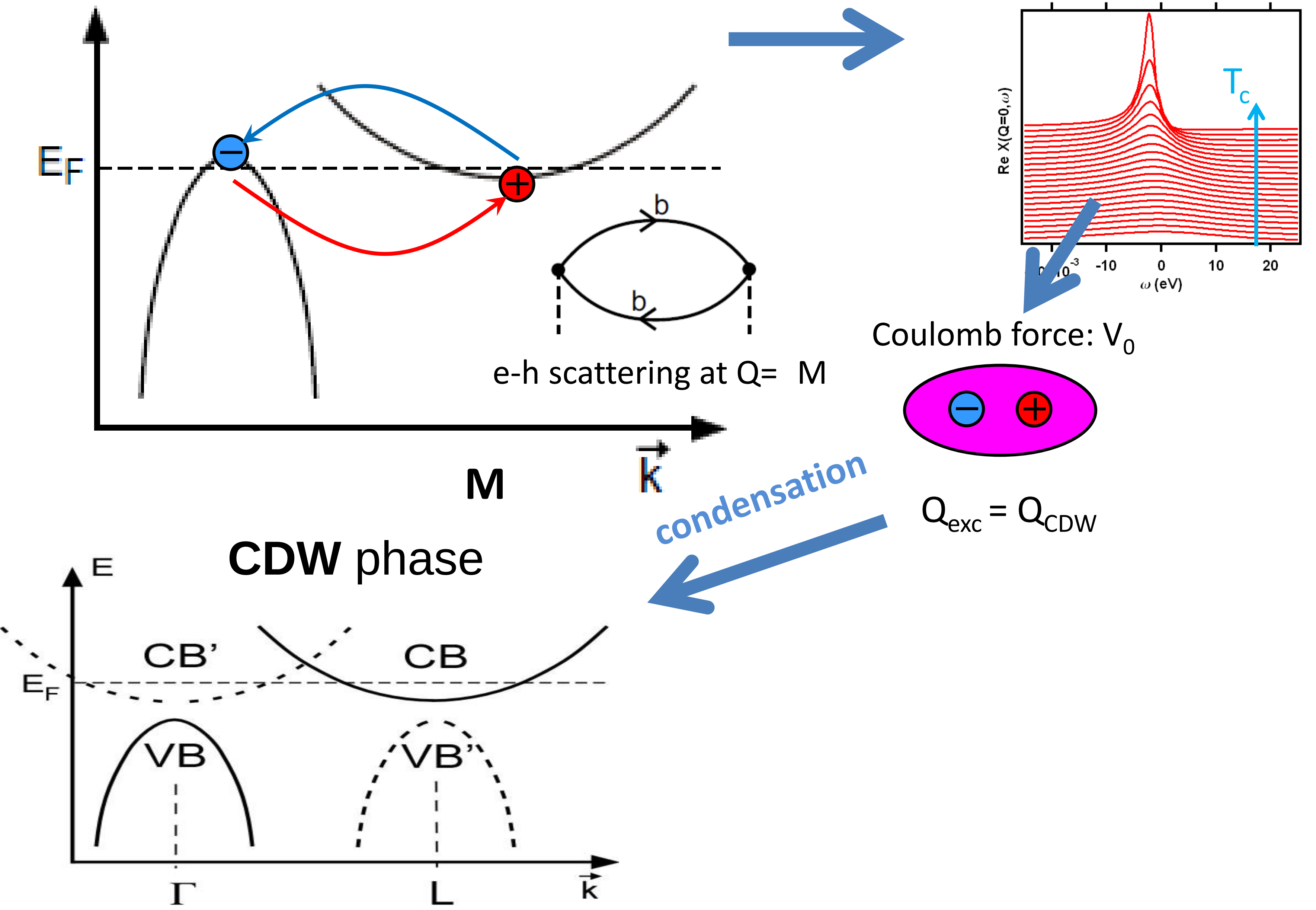
From electron-hole fluctuations to the CDW phase



e-h scattering at Q= M



From electron-hole fluctuations to the CDW phase



e-h scattering at Q= M

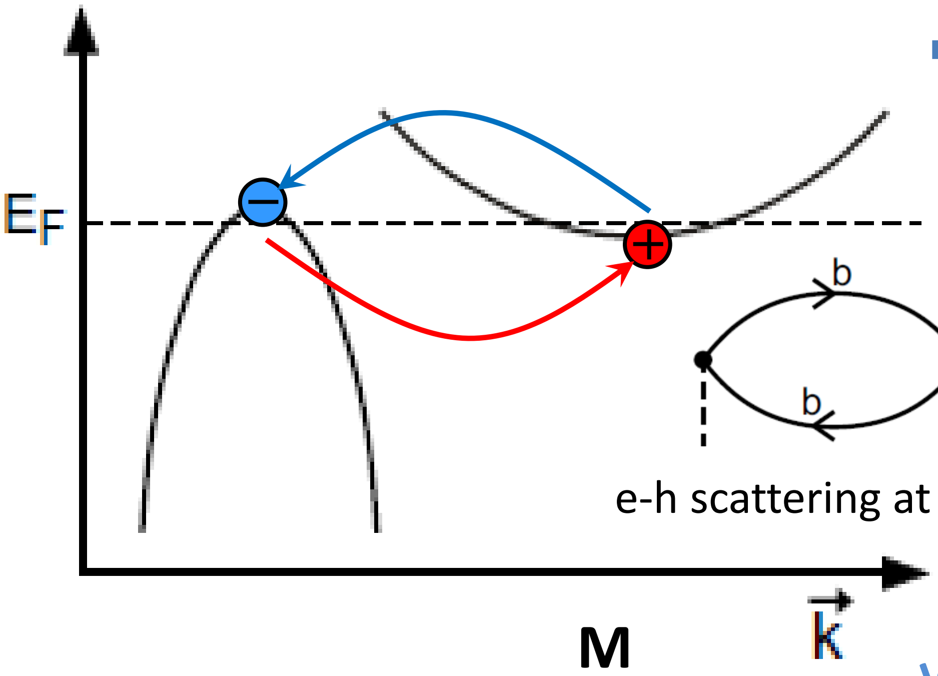
Coulomb force: V_0

$Q_{exc} = Q_{CDW}$

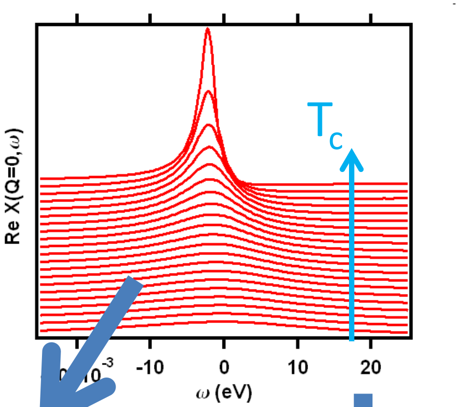
condensation

CDW phase

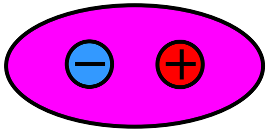
From electron-hole fluctuations to the CDW phase



e-h scattering at Q= M



Coulomb force: V_0

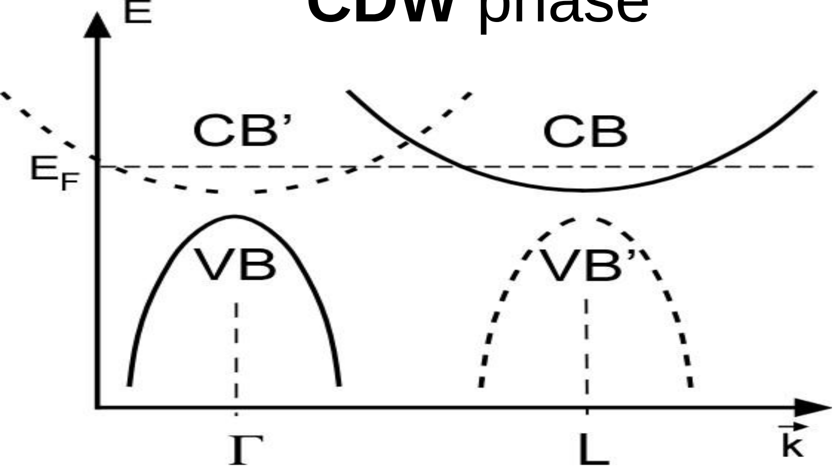


$Q_{exc} = Q_{CDW}$

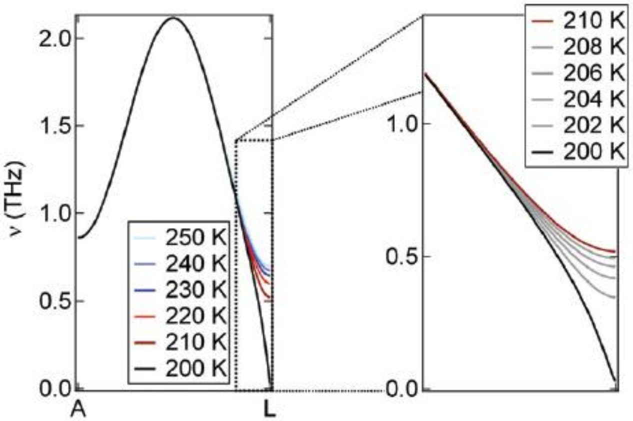
el-ph coupling g

condensation

CDW phase



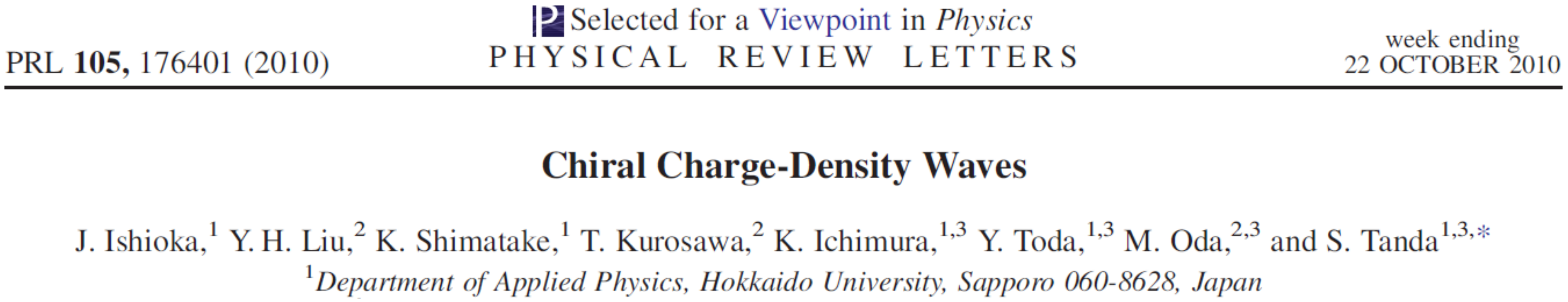
PLD



Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

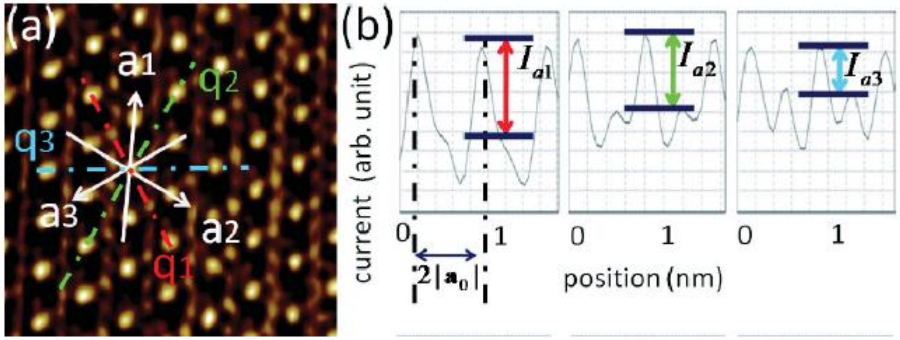
Scanning tunneling microscopy: chiral CDW phase

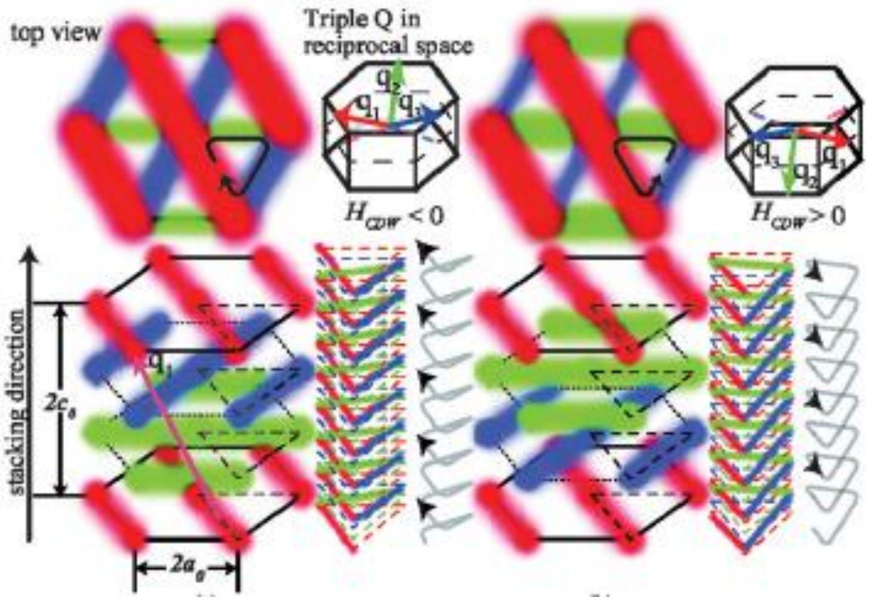


PRL **105,** 176401 (2010) Selected for a Viewpoint in *Physics*
PHYSICAL REVIEW LETTERS
week ending
22 OCTOBER 2010

Chiral Charge-Density Waves

J. Ishioka,[1] Y. H. Liu,[2] K. Shimatake,[1] T. Kurosawa,[2] K. Ichimura,[1,3] Y. Toda,[1,3] M. Oda,[2,3] and S. Tanda[1,3,*]
[1]*Department of Applied Physics, Hokkaido University, Sapporo 060-8628, Japan*





Ordered distribution of STM intensity for different CDW Q-vectors

-> chiral CDW phase!

EFKM model for the chiral CDW phase

Extended Falicov-Kimball model with electron-phonon interaction (1st order) and (cubic and quartic) phonon-phonon interaction

$$n_i(\mathbf{Q}_\alpha) = A\cos(\mathbf{Q}_\alpha \mathbf{R}_i + \theta_\alpha)$$

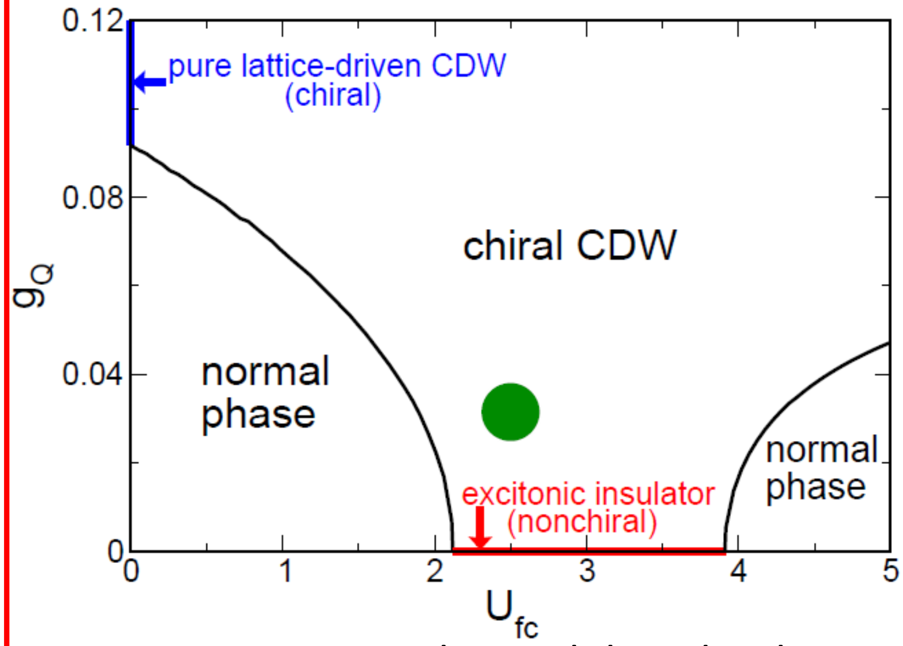
CDW state at low temperature with PLD.

Charge order: excitonic insulator & PLD.

Phase of the CDW is locked to that of the PLD.

Phonon-phonon interaction (quartic term) induces 3 different phases.

B. Zenker, H. Fehske, C.M. *et al.*, arXiv (2013)

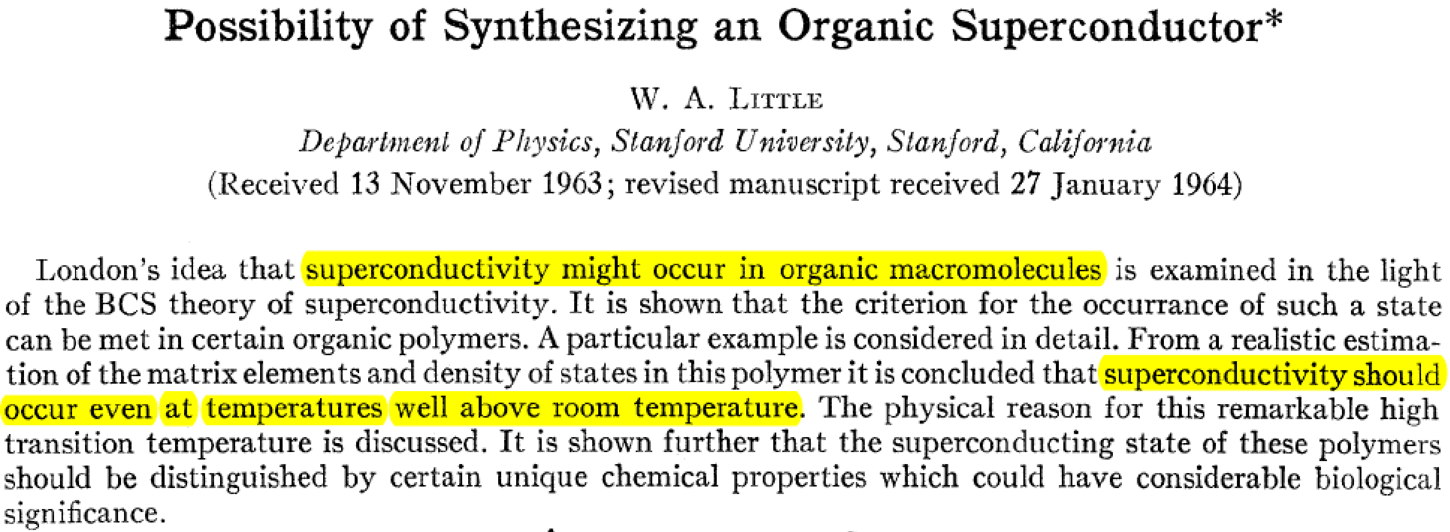


Lattice DOFs essential to stabilize chiral CDW within the extended Falicov Kimball model

Outline

- The phase diagram of $TiSe_2$
- ARPES data of $TiSe_2$
- The excitonic insulator model: mean-field approach
- Electron-hole instability: fluctuation phase and ARPES
- Other experiment on $TiSe_2$: a chiral CDW phase
- Outlook

Exciton mediated superconductivity??

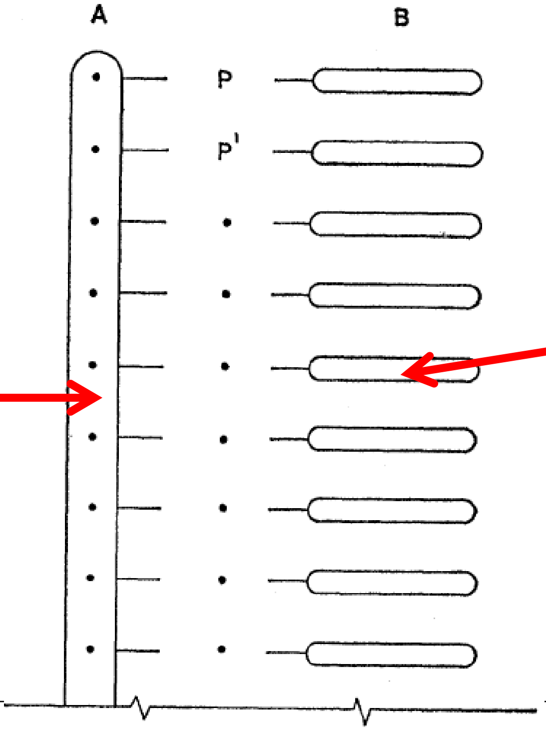


Possibility of Synthesizing an Organic Superconductor*

W. A. Little
Department of Physics, Stanford University, Stanford, California

(Received 13 November 1963; revised manuscript received 27 January 1964)

London's idea that superconductivity might occur in organic macromolecules is examined in the light of the BCS theory of superconductivity. It is shown that the criterion for the occurrance of such a state can be met in certain organic polymers. A particular example is considered in detail. From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature. The physical reason for this remarkable high transition temperature is discussed. It is shown further that the superconducting state of these polymers should be distinguished by certain unique chemical properties which could have considerable biological significance.



„spine“: electron reservoir for superconductivity

highly polarizeable (= e-h pair excitations) molecules for mediating attractive Coulomb force (overscreening)

The end

Thank you for your attention!