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Muntaser Naamneh:: SIS beamline @ Swiss Light Source :: Paul Scherrer Institut

# Phase mixture and pseudogap behavior in the bismuthate high Tc superconductors

Empa Postdocs-II & PSI-Fellow II-3i Retreat

Empa Dübendorf, 21.09.2018

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# Acknowledgments


- **PLD + ARPES team (PSI):** N. Plumb, M. Radovic, J. Jandke , J. Ma, M. Yao, M. Shi, J. Mesot

- **Materials:** D. Gawryluk, T. Shang, M. Medarde, K. Conder, E. Pomjakushina

- **Theory:** Y. Wang, S. Li, S. Johnston (U. Tennessee Knoxville), T. Berlijn (Oak Ridge Nat'l Lab), M. Müller (PSI)

- **Raman:** J. Teyssier, A. Stucky, D. van der Marel (U. Geneva)

European Commission

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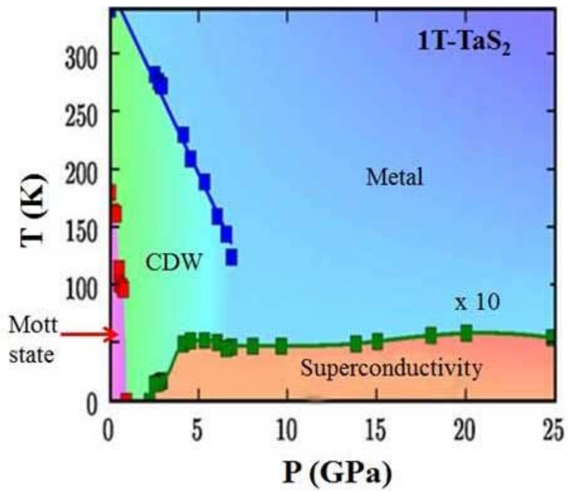
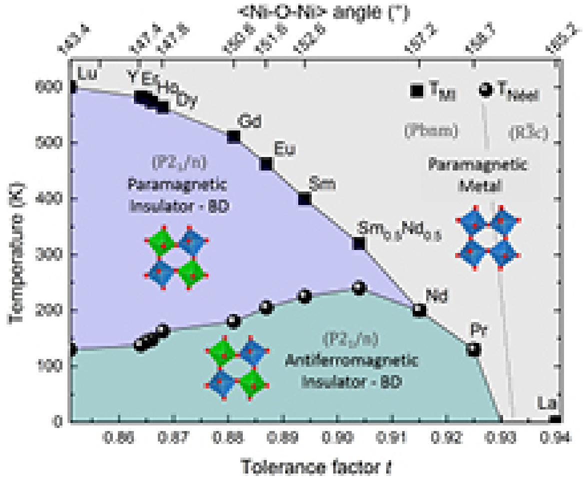
# Strongly correlated systems

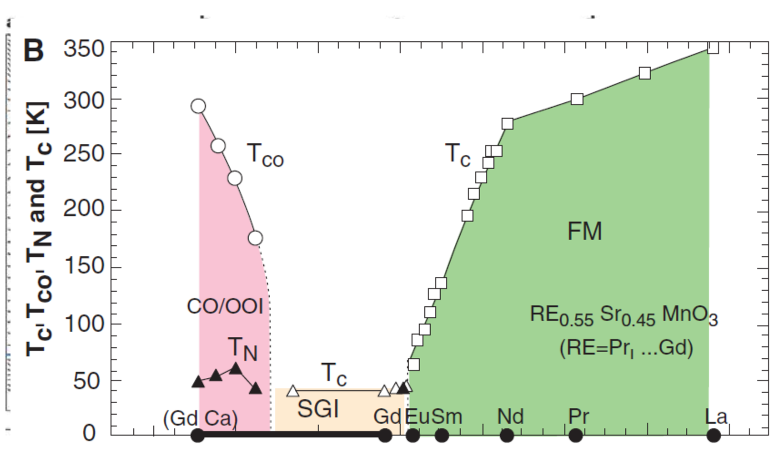
## Transition metal dichalcogenides




## Rare earth nickelates

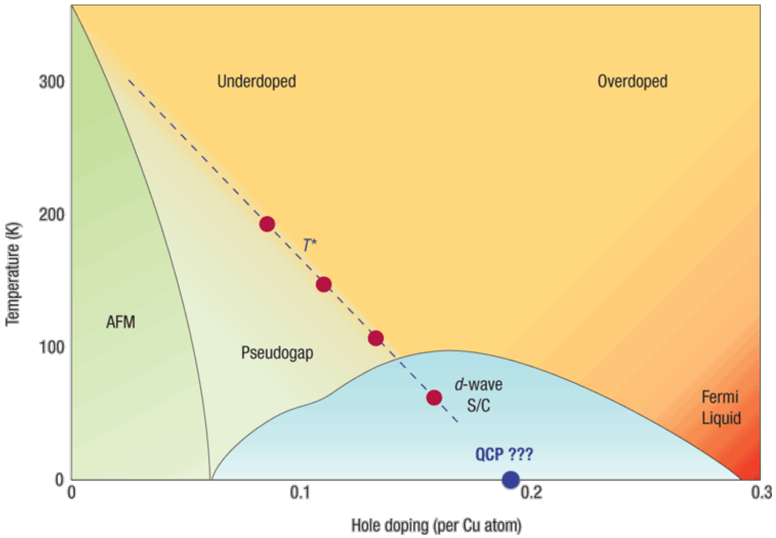



## Manganites



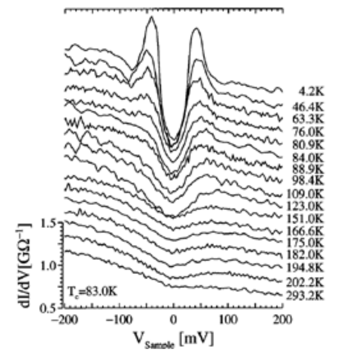

*Nature* **volume438**, pages474–478 (24 November 2005)

## Unconventional superconductors



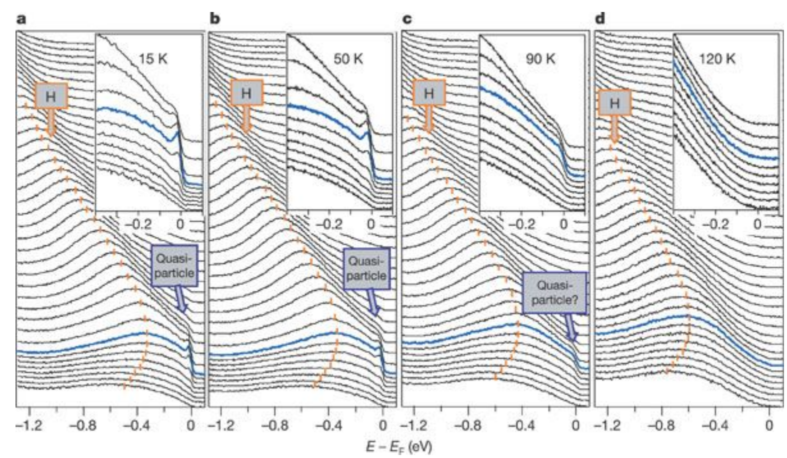
# Pseudogap

**Pseudogap term is used in all of this materials to describe a suppression of spectral weight with no obvious symmetry breaking.**



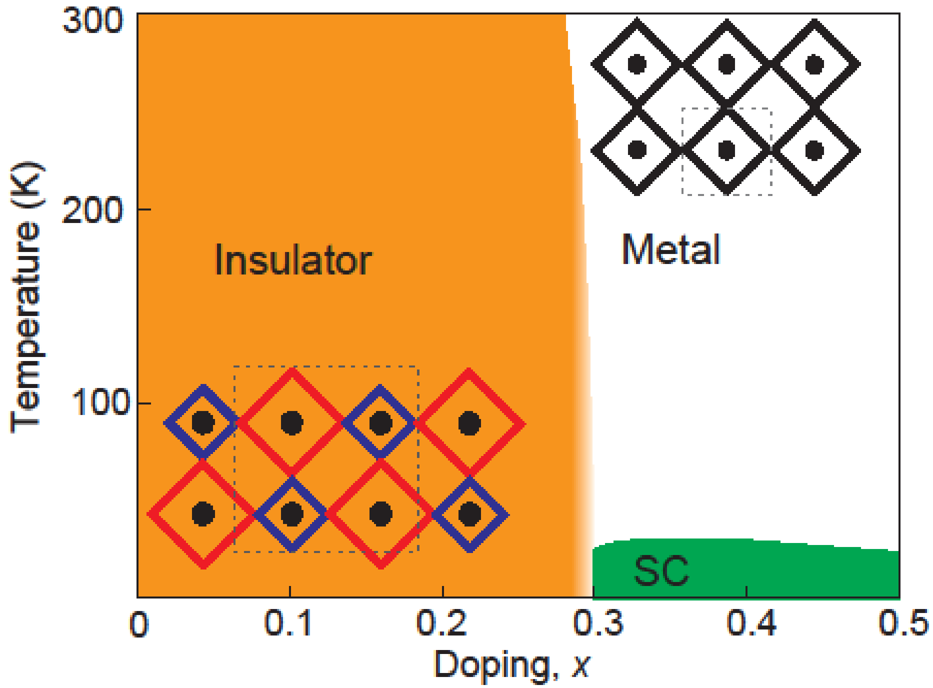

Phys. Rev. Lett. **80**, 149, 1998

**What is the origin of the pseudogap?**




*Nature* **volume438**, pages474–478 (24 November 2005)

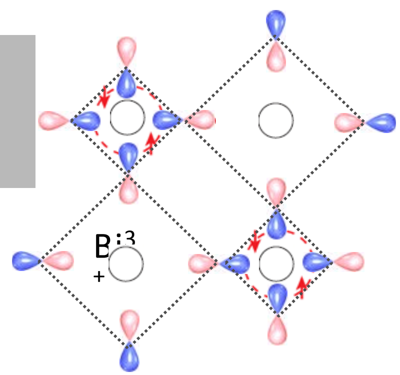
# $Ba_{1-x}K_xBiO_3$ phase diagram

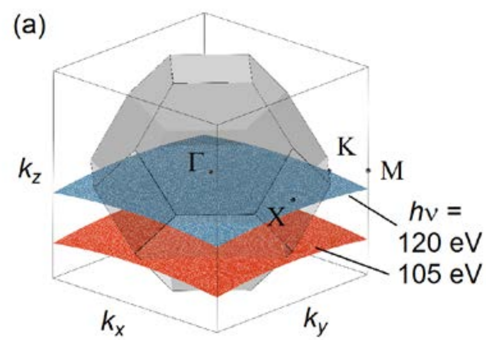


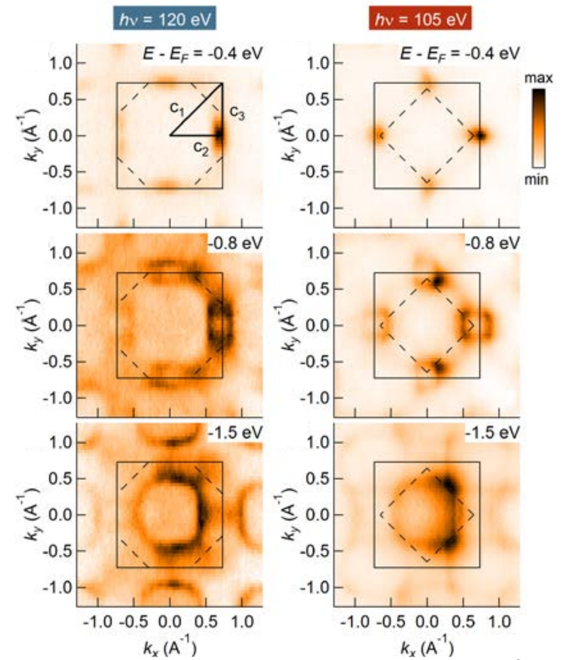

- 3D perovskite structure.
- Parent compound insulating behavior is linked to lattice distortions in the form of breathing mode
- SC emerges with doping. $T_c$ = 32 - 34 K (x ~ 0.38) from insulating parent compound.
- No magnetic order. SC is phonon-mediated (isotope shift in $T_c$)

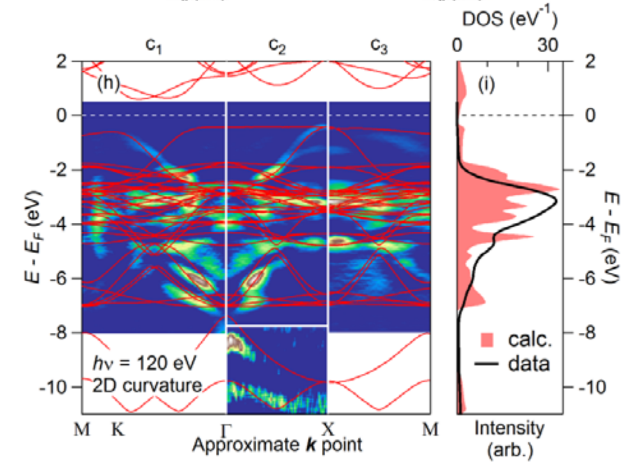
An overview: A. W. Sleight, Physica C 514, 152 (2015)

# Electronic structure of the Parent Compound
# Freezed lattice of bipolarons

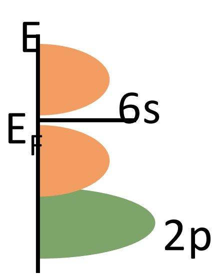


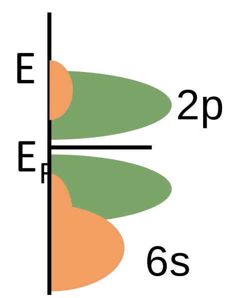



- The Brillouin zone is folded due to breathing distortions of insulating.
- The BaBiO3 insulator is negative charge transfer insulator, similar to the nickelates.

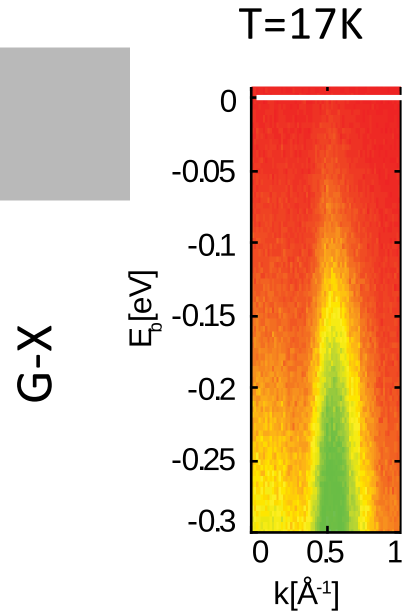


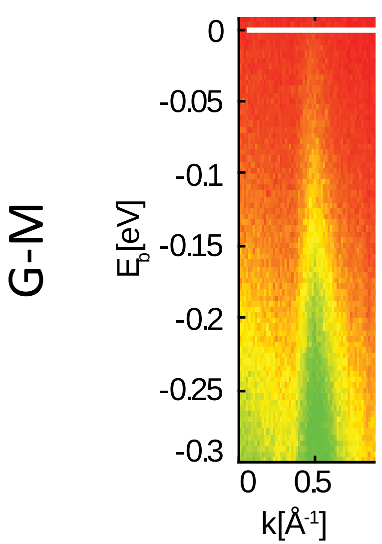



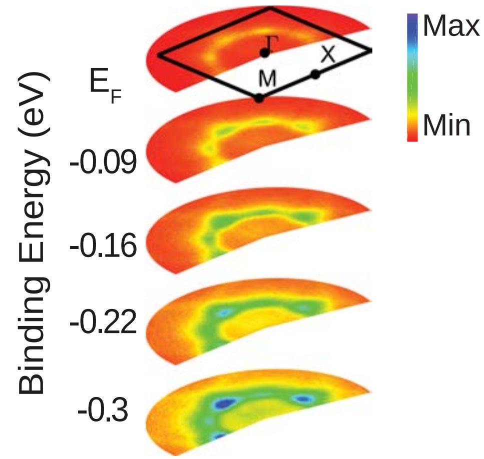

Foyevtsova, Sawatzky, et al., PRB 91, 121114(R) (2015)

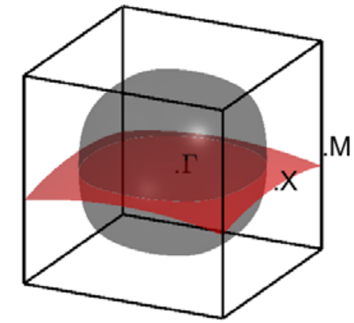
Plumb et al., PRL 117, 037002 (2016)

# Fermi surface ($x$ = 0.34)

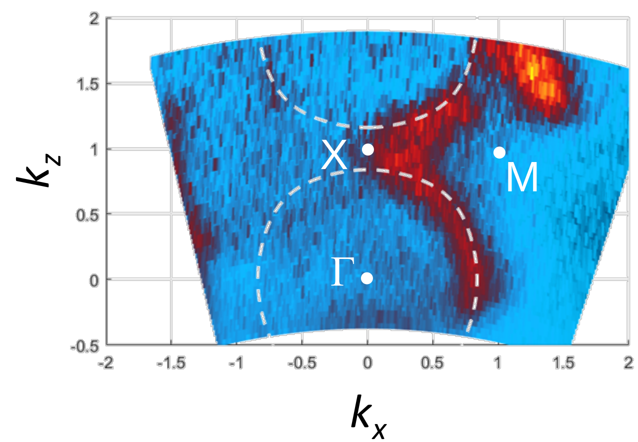


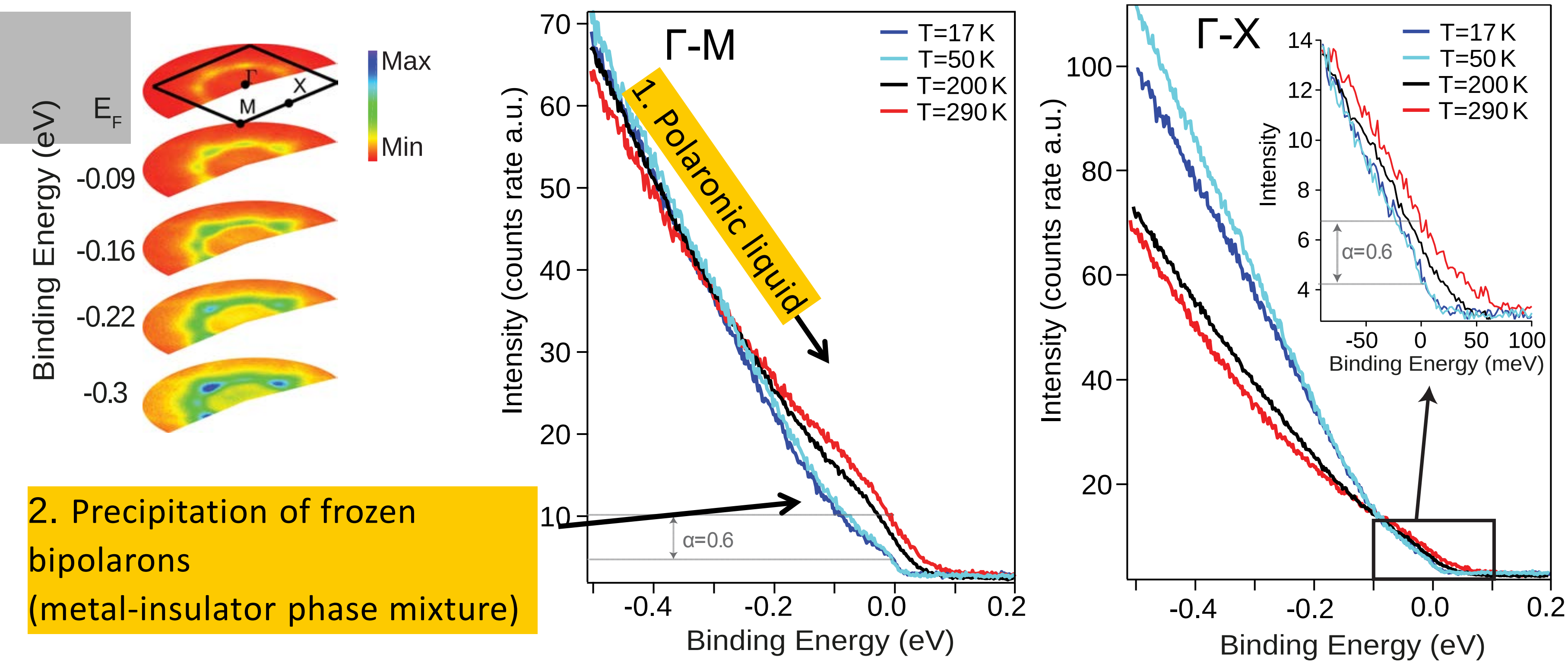

TB: Sahrakorpi et al,
PRB 61, 7388 (2000).




At temperatures below Tp, a spectral weight near Ef is reduced

Naamneh et al., arxiv:1808.06135

# Electronic structure of BKBO: pseudogap



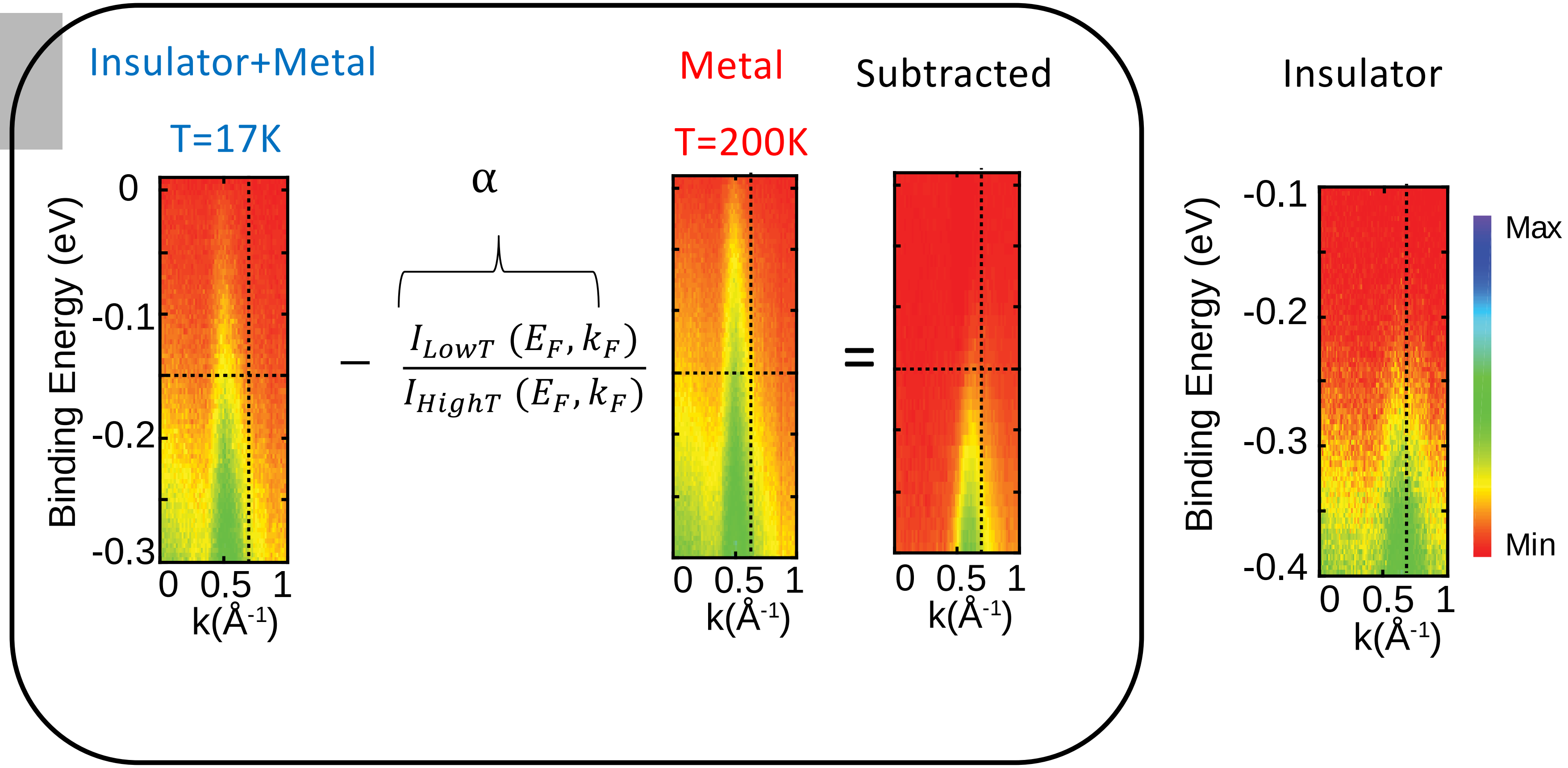

- Quasiparticle peak is absent.
- The spectral weight is suppressed below Tp.
- The reduction is isotropic at Ef.
- The redistribution of the weight is anisotropic at deep binding energies.

See also
-Karlow et al., PRB 48, 6499 (1993)
-Chainani et al., PRB 64, 180509 (2001)

# Phase separation- cuts

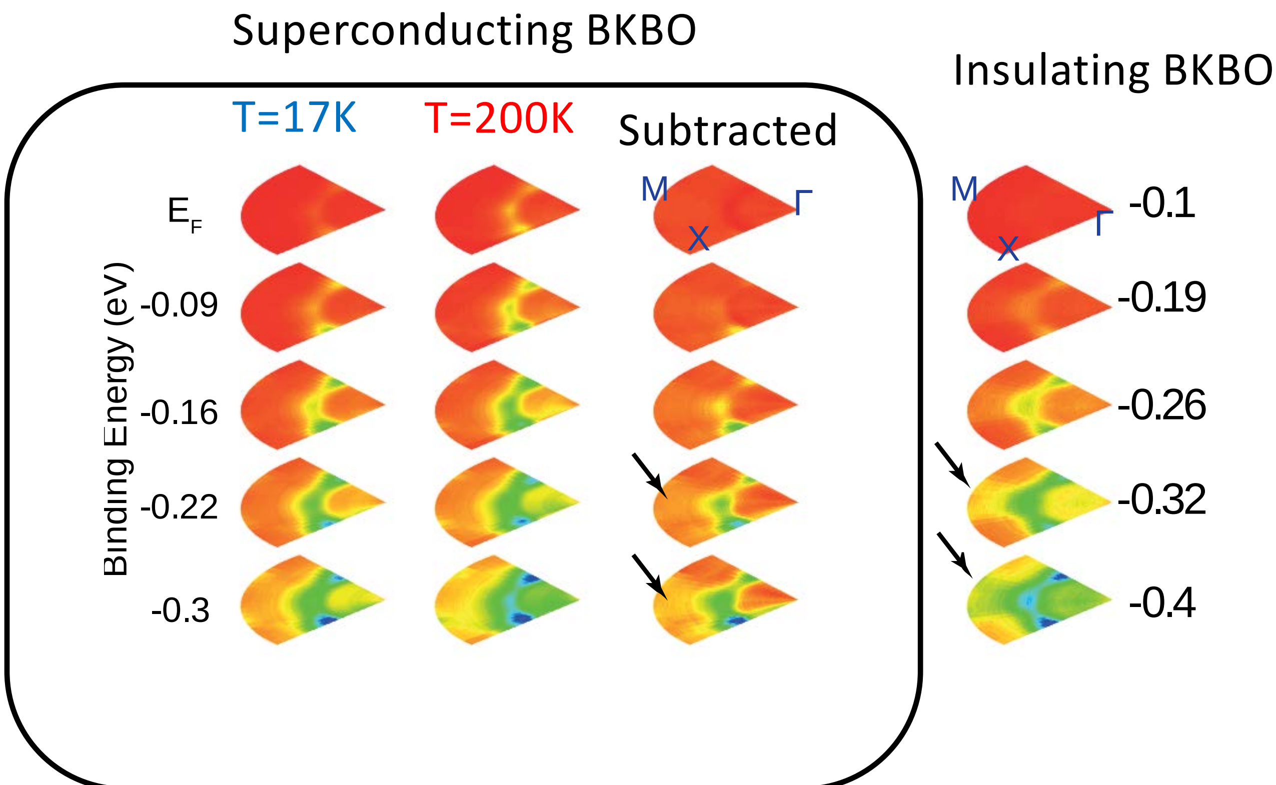
Superconducting BKBO

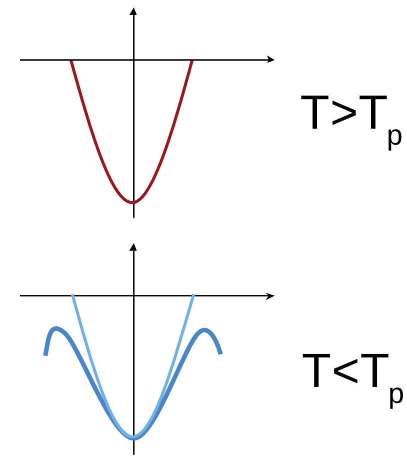
Insulating BKBO

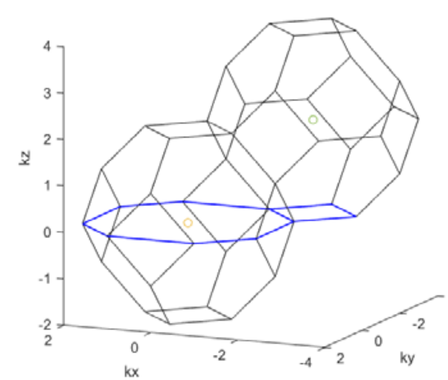



Naamneh et al., arxiv:1808.06135

# Phase separation-Fermi Surface



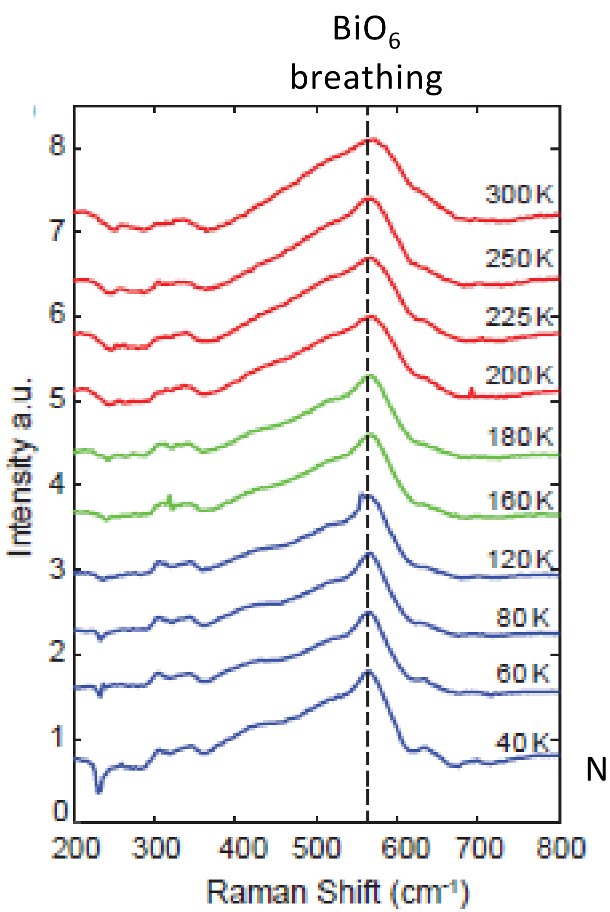




Single scaling value.

Naamneh et al., arxiv:1808.06135

# Raman scattering




Naamneh et al., arxiv:1808.06135

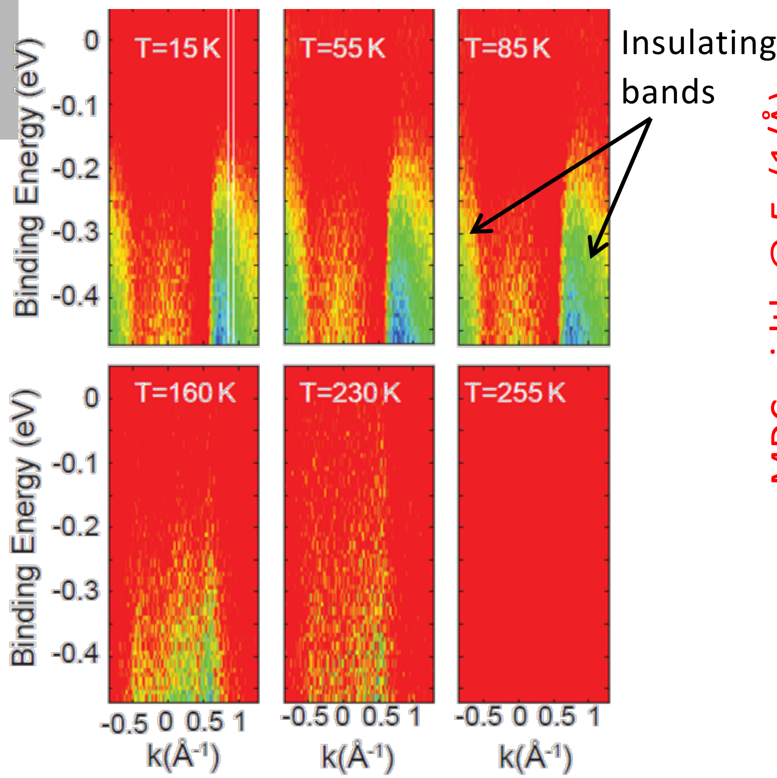
- Breathing distortion peak at all temperatures, **in contrast with neutrons**
- → Local distortions embedded/fluctuating in a different global symmetry
- Similar findings in nickelates:

➢ Li et al., Adv. Electron. Mater. 2, 1500261 (2016).
➢ Shamblin et al, Nat. Commun. 9, 86 (2018).

Little happening in structural probes.
Why is there an *electronic* transition to phase separation?

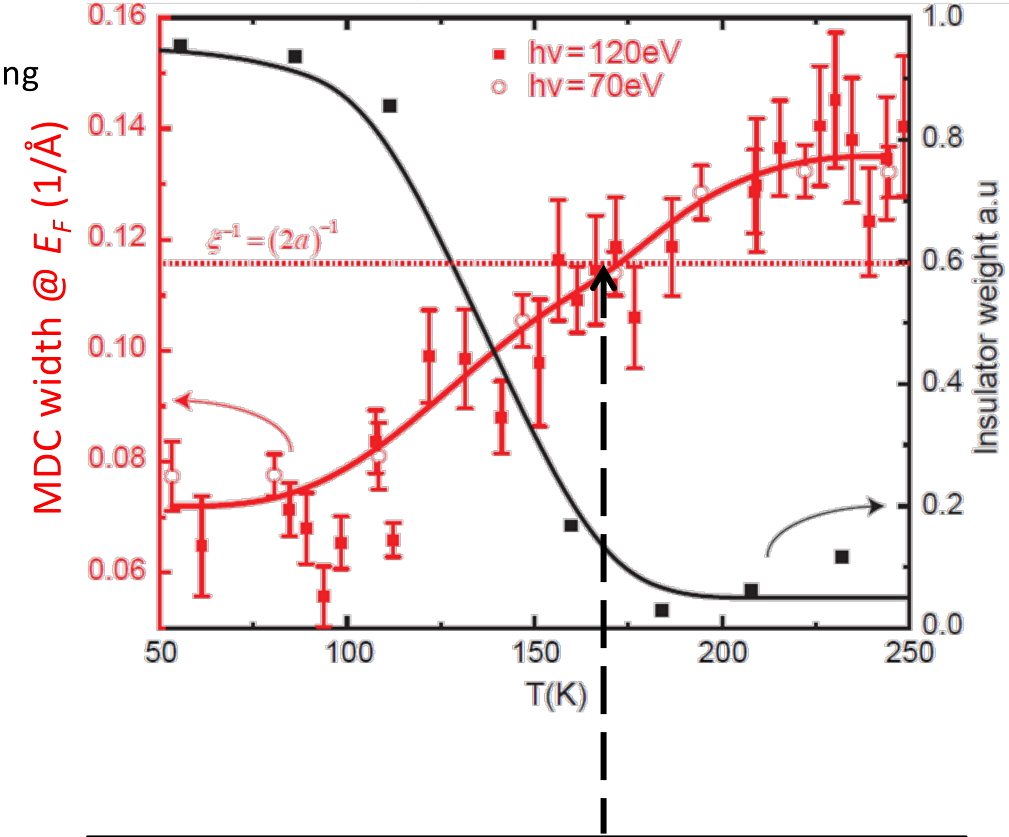
# ARPES view of electronic scattering

Subtracted spectra



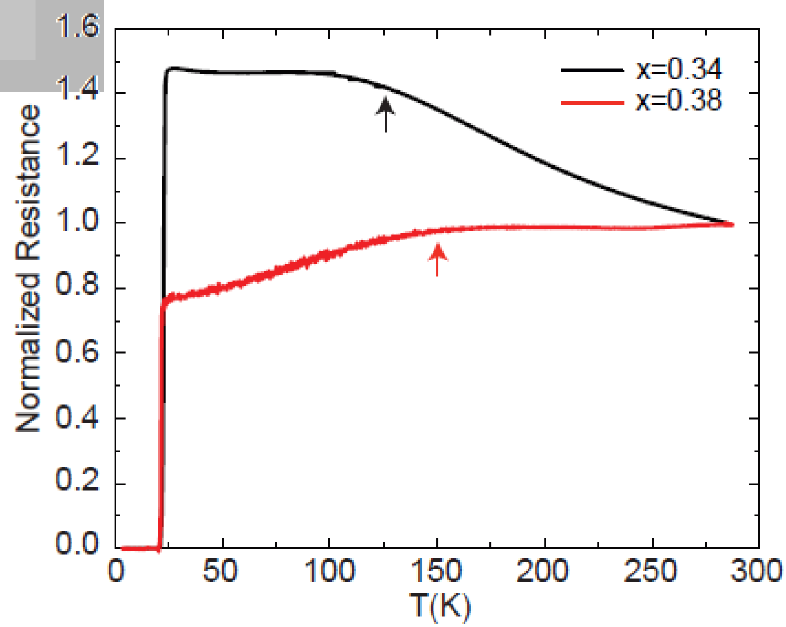

Naamneh et al., arxiv:1808.06135

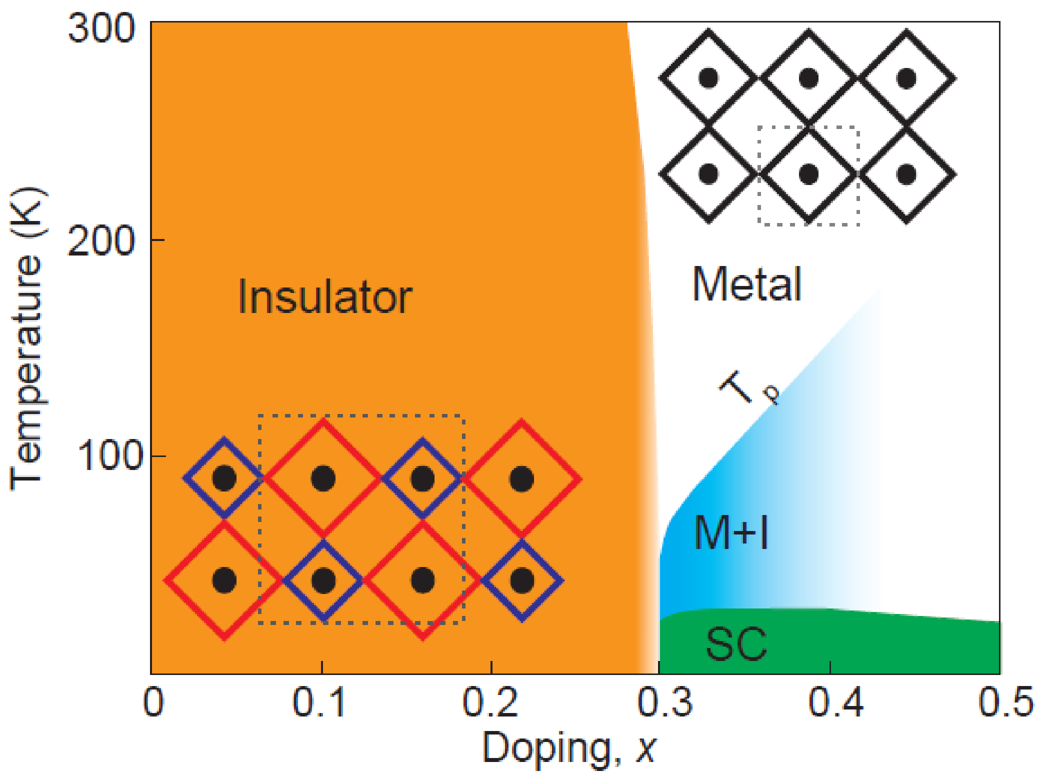
At X point (near vHs)




Onset when scattering at $E_F$ corresponds to **electron mean free path = 2*a*.**
→ *Formation of insulator impeded by (lack of) electronic coherence.*

# Doping dependence of $T_p$



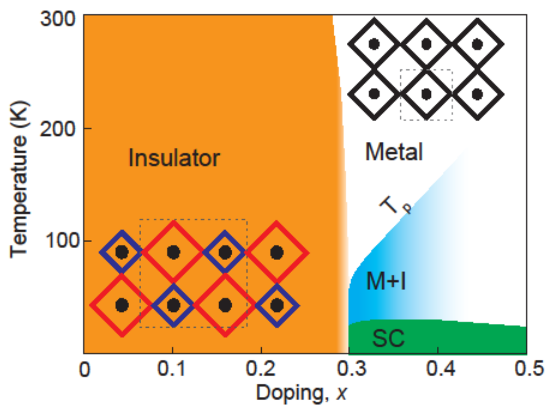



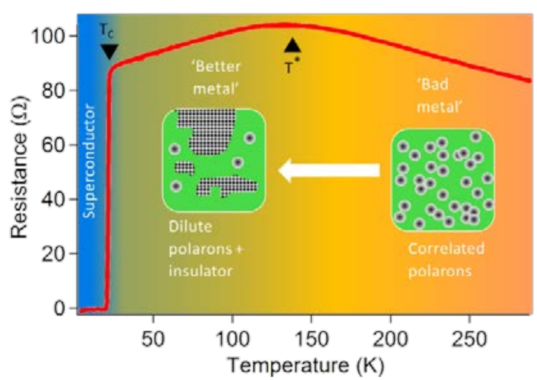

Naïve picture: Higher doping → lower $T_p$ (further from insulator) … WRONG!

Scattering picture: Higher doping → less scattering → higher $T_p$ … OBSERVED!

# Conclusions

- Depending on definition, we observe two types of PG:
  - Appear below Tp and be regarded as true bandgap whose origin and underlying symmetry had been obscured by phase separation.
  - Broad energy suppression approaching Ef persisting to room temperature and characterized by an absence of QP peak.
- Both pseudogaps stem from bi-polarons interactions.
- The phase separation is driven by scattering rather than change in the lattice.



# Very dispersive bands with no QPs?

- In Su-Schrieffer-Heeger model, (bi)polaron “wants” to hop.
- Strong coupling doesn’t necessarily imply high mass.

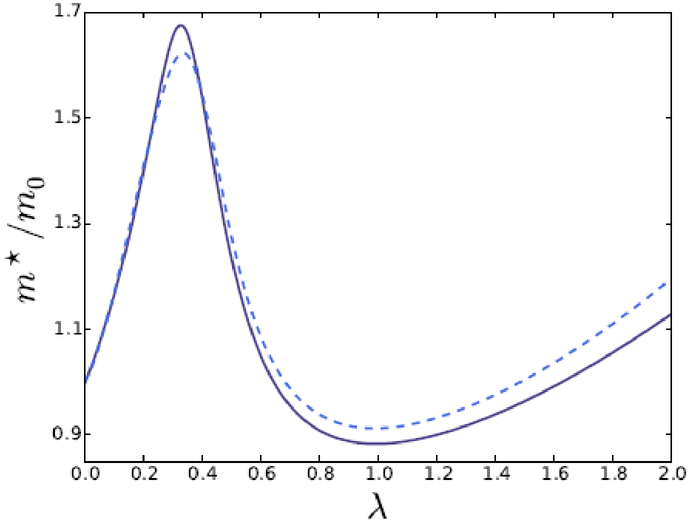



FIG. 2. (Color online) Dependence of the effective mass of the low-energy bipolaron on $\lambda$, for $U = 0$ and $\Omega = 3.0$. $m_0 = 2m_e$ is twice the free electron mass. The bipolaron’s effective mass is defined as $m^* = \left(\frac{\partial^2 E_{BP}(K)}{\partial K^2}\right)^{-1}\Big|_{K=K_{GS}}$. The solid (dashed) lines are VED (MA) results. Note that $m^* \sim 2m_e$ in the strongly coupled regime, $\lambda > 1$.

Sous et al., arxiv: 1805.06109

# Unique tools at the SIS beamline

S.F. Liu, W.T. Fu / Materials Research Bulletin 36 (2001) 1505–1512

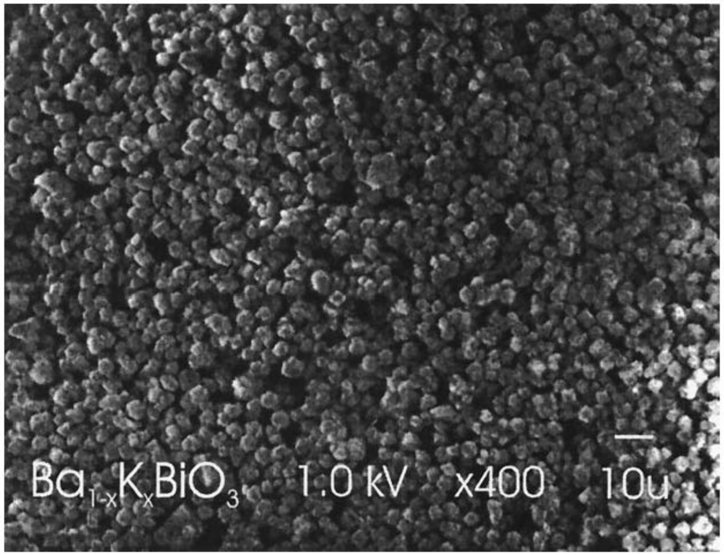
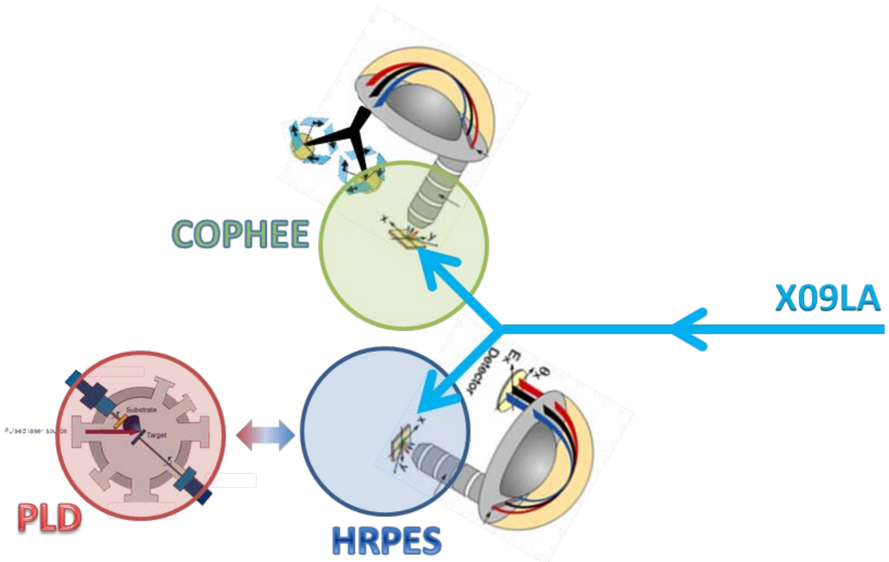
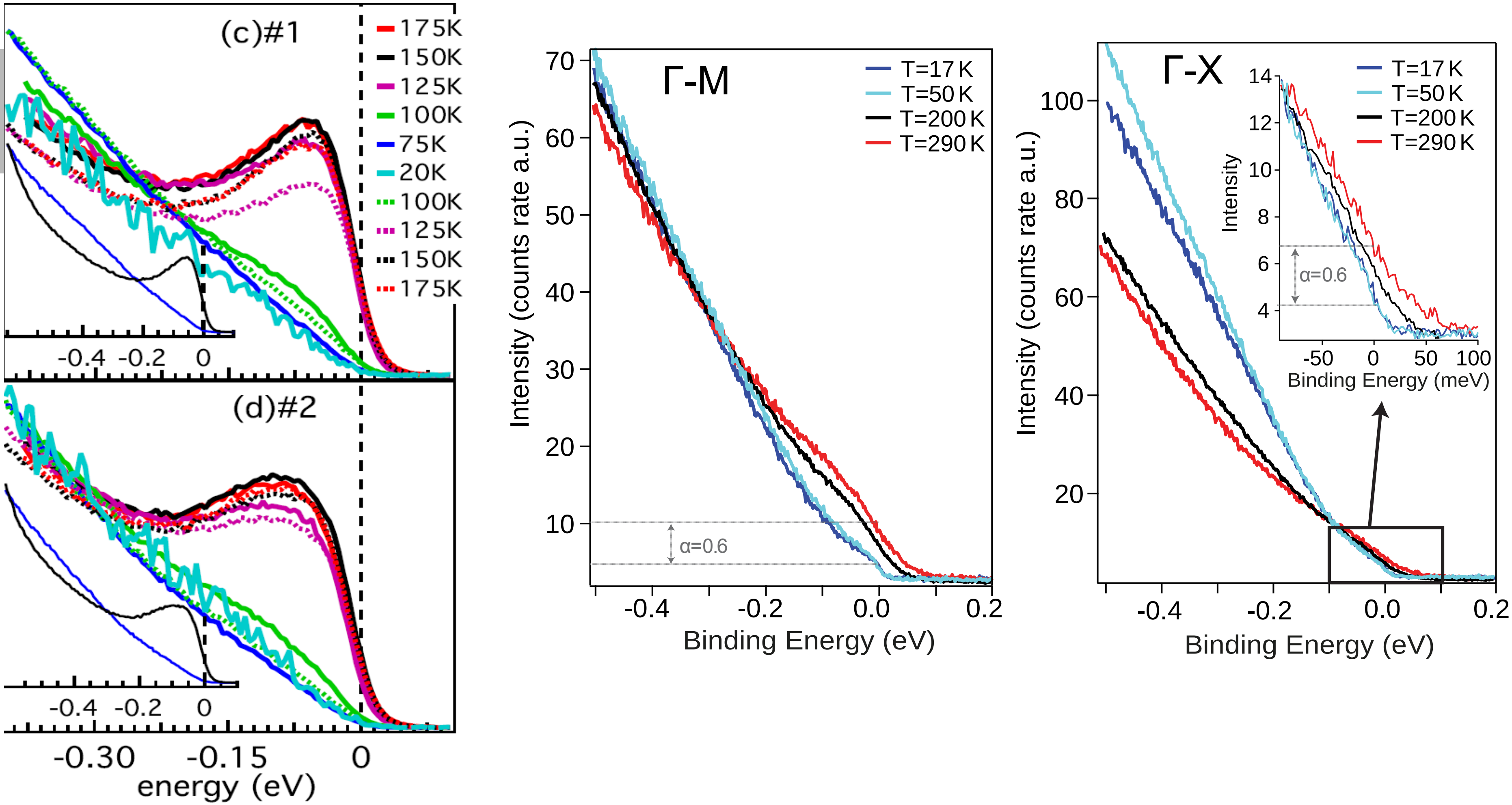



Fig. 3. SEM photograph of $Ba_{1-x}K_xBiO_3$.




Our approach: *In situ* spectroscopy on thin films

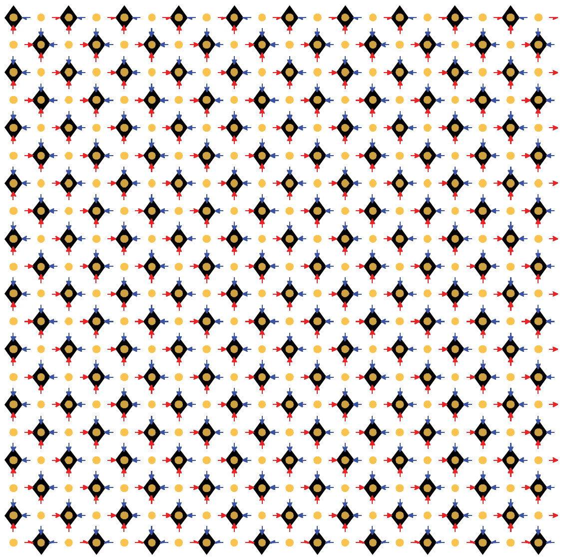
# Electronic structure of BKBO: pseudogap




R. S. Dhaka et al, Phys. Rev. B 92, 035127 (2015)

Naamneh et al., arxiv:1808.06135

# Phase separation simulation-Model



$$H = -t_{sp}\sum_{\mathbf{r},\sigma}(1-\alpha x_{\mathbf{r}})(s^{\dagger}_{\mathbf{r},\sigma}p_{\mathbf{r},x,\sigma}+h.c.) - t_{sp}\sum_{\mathbf{r},\sigma}(1-\alpha y_{\mathbf{r}})(s^{\dagger}_{\mathbf{r},\sigma}p_{\mathbf{r},y,\sigma}+h.c.)$$

$$+t_{sp}\sum_{\mathbf{r},\sigma}(1+\alpha x_{\mathbf{r}})(s^{\dagger}_{\mathbf{r}+\mathbf{a},\sigma}p_{\mathbf{r},x,\sigma}+h.c.) + t_{sp}\sum_{\mathbf{r},\sigma}(1+\alpha y_{\mathbf{r}})(s^{\dagger}_{\mathbf{r}+\mathbf{b},\sigma}p_{\mathbf{r},y,\sigma}+h.c$$

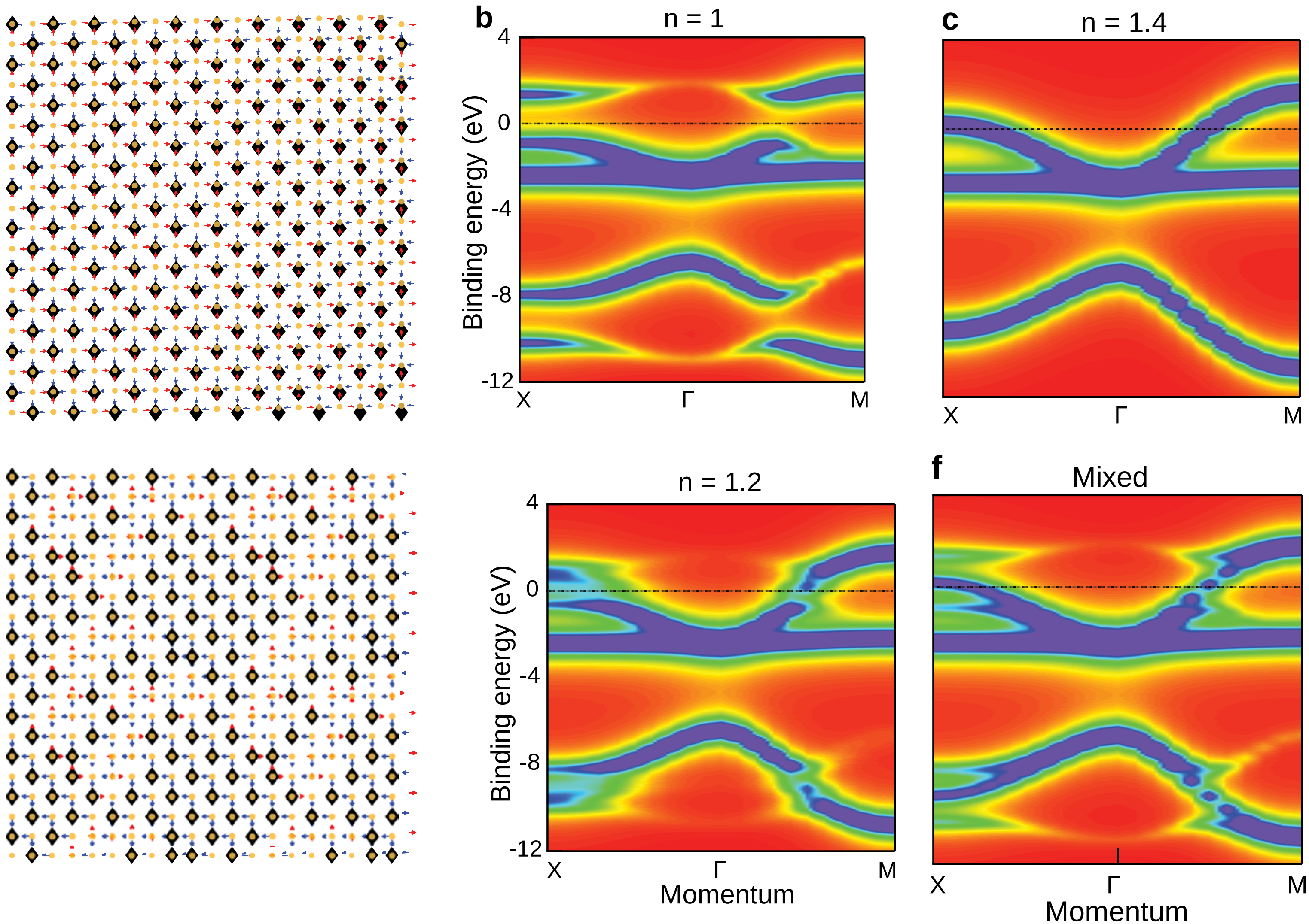
$$+t_{pp}\sum_{\mathbf{r},\sigma}(p^{\dagger}_{\mathbf{r},x,\sigma}p_{\mathbf{r},y,\sigma} - p^{\dagger}_{\mathbf{r},y,\sigma}p_{\mathbf{r}-\mathbf{a},x,\sigma} + p^{\dagger}_{\mathbf{r}-\mathbf{a},x,\sigma}p_{\mathbf{r}-\mathbf{b},y,\sigma} - p^{\dagger}_{\mathbf{r}-\mathbf{b},y,\sigma}p_{\mathbf{r},x,\sigma})$$

$$+\sum_{\mathbf{r},\sigma}(\epsilon_s\hat{n}^{s}_{\mathbf{r},\sigma} + \epsilon_p\hat{n}^{p_x}_{\mathbf{r},\sigma} + \epsilon_p\hat{n}^{p_y}_{\mathbf{r},\sigma}) + \sum_{\mathbf{r}}(Kx^2_{\mathbf{r}} + Ky^2_{\mathbf{r}}).$$

Minimizing the energy of the system with correspond to the O displacement.

$$A(\mathbf{k},\omega) = \frac{1}{2\pi}\sum_{m,\gamma,\sigma}\frac{|\langle\mathbf{k},\gamma\mid\Psi_{m,\sigma}\rangle|^2}{\omega - E_{m,\sigma} + i\delta},$$

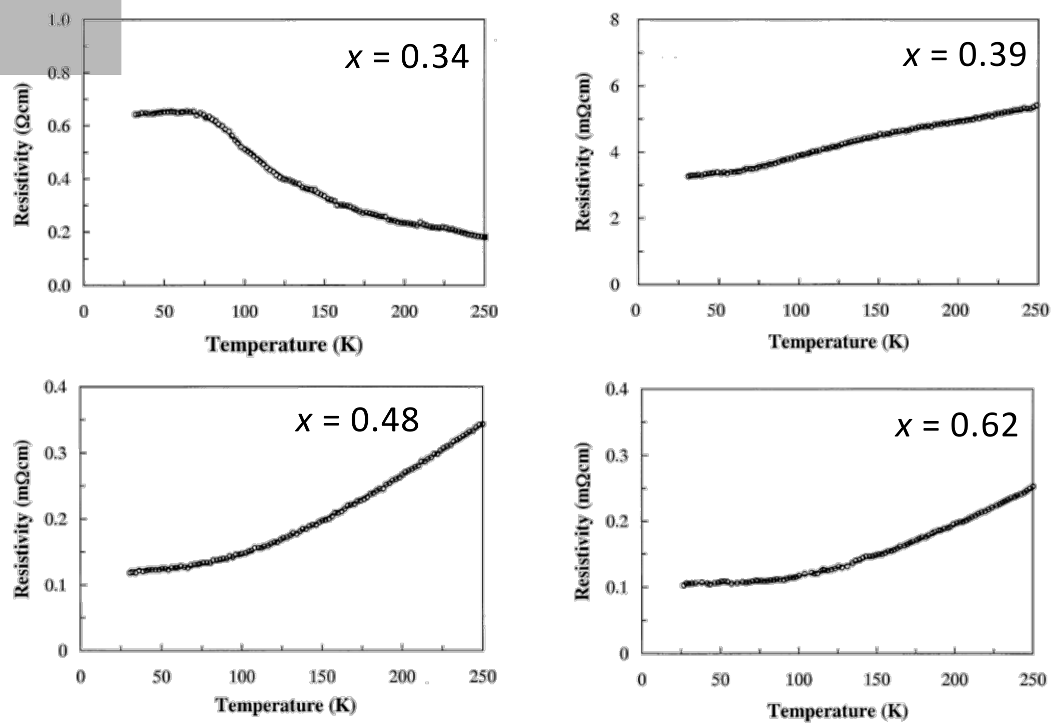
# Phase separation simulation-Results




Intermediate doping behaves as a suppression of metallic and insulator.

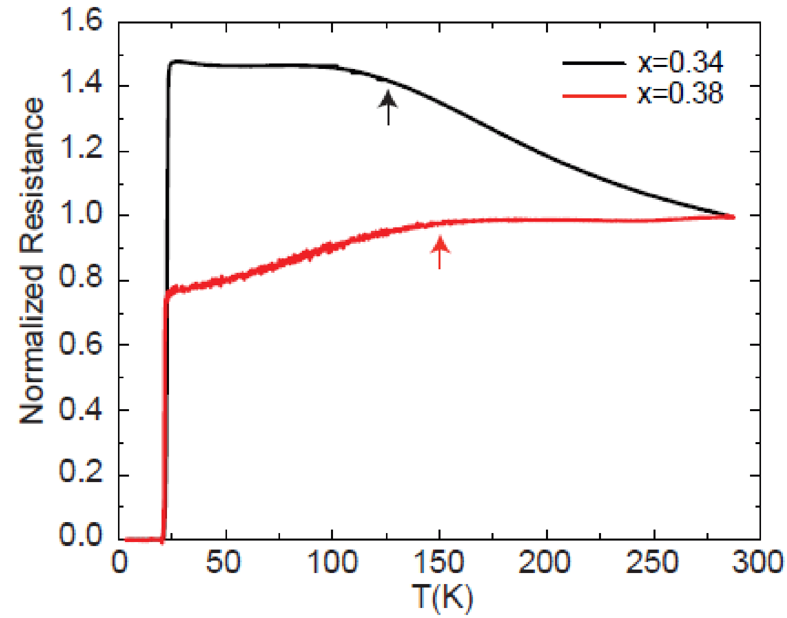
# Doped “normal state” transport

**Single crystals**




Nagata et al., J. Phys. Chem. Solids 60, 1933 (1999).

**Our films**




Naamneh et al., arxiv:1808.06135

# Same signatures in single crystals

## k-integrated PES

Chainini et al., PRB 64, 180509(R) (2001).

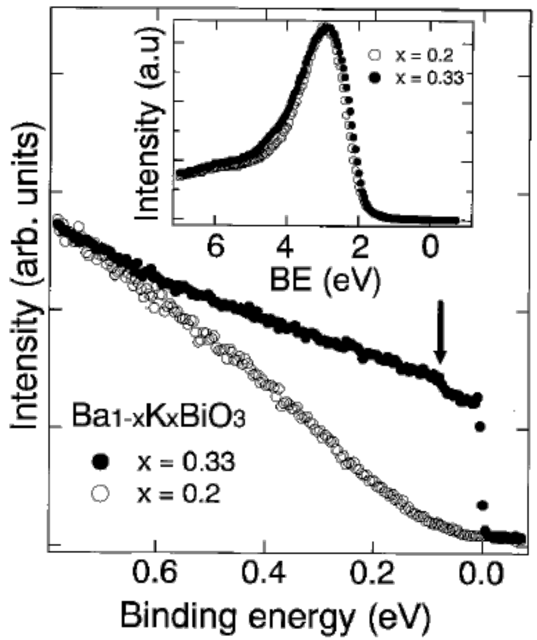
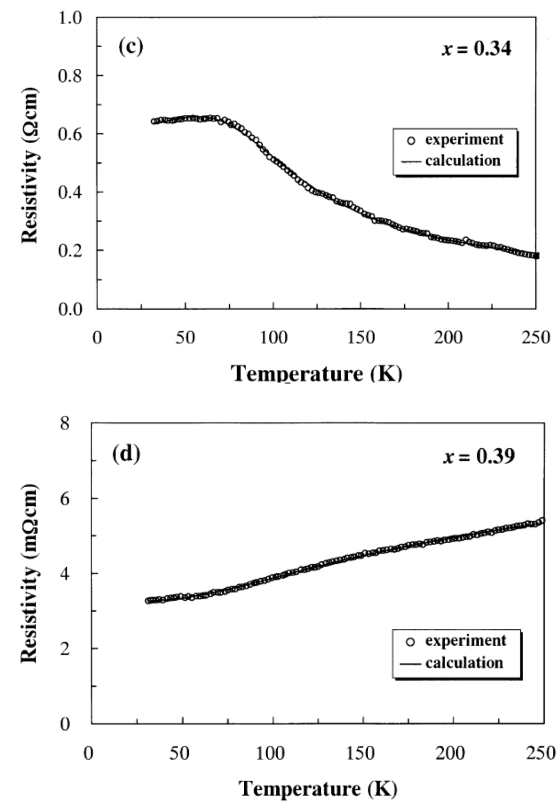



FIG. 3. The valence band spectra of $Ba_{1-x}K_xBiO_3$ ($x=0.2$ and 0.33) showing changes across the semiconductor-metal transition and a pseudogap over ~70 meV (arrow) for $x=0.33$ at 5.3 K. The superconducting transition is not clear here due to the larger step size used. The inset shows the full valence band spectra.

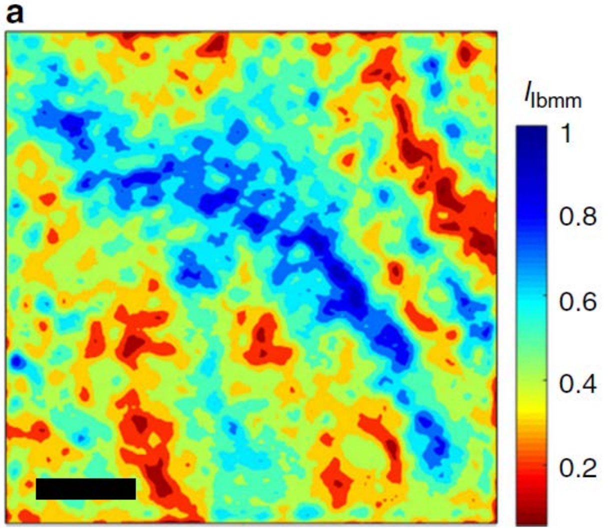
## Transport

*Y. Nagata et al. / Journal of Physics and Chemistry of Solids 60 (1999) 1933–1942*



# TEM: Phase separation in BaPBiO3

structural polymorphs is detected by TEM in superconducting sample of $BaPb_{1-x}Bi_xO3$.



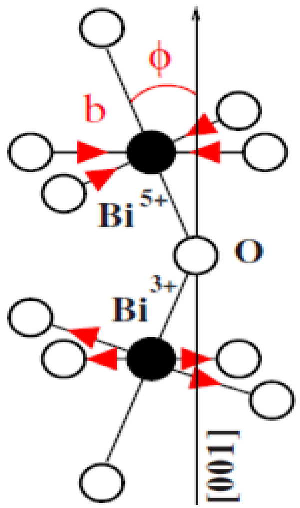

10nm

The system is ordered in nano-stripes having different structures, tetragonal and orthorhombic.

Maximum Tc occurs when the superconducting coherence length matches the width of the partially disordered stripes.

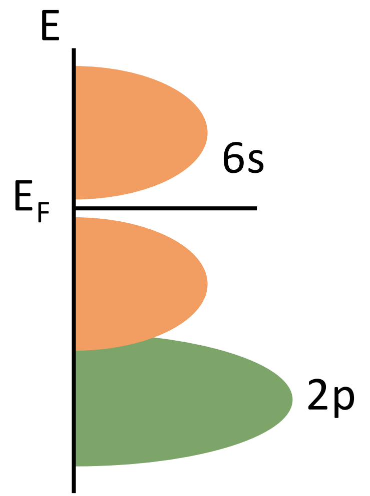
Giraldo-Gallo, P. el al, Nat. Commun. **6**, 8231 (2015).

# Debates surrounding insulating phase



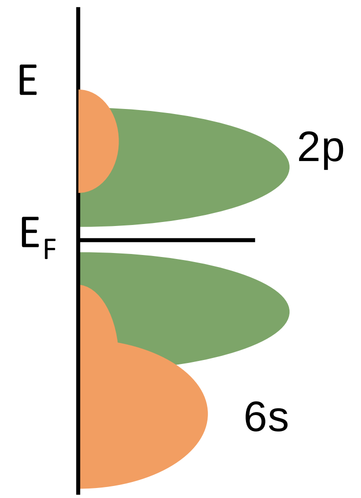

Picture: Franchini et al., PRB 81, 085213 (2010)

Classical picture
Bi charge order




vs.

Alternative proposal
"Bond disproportionation"

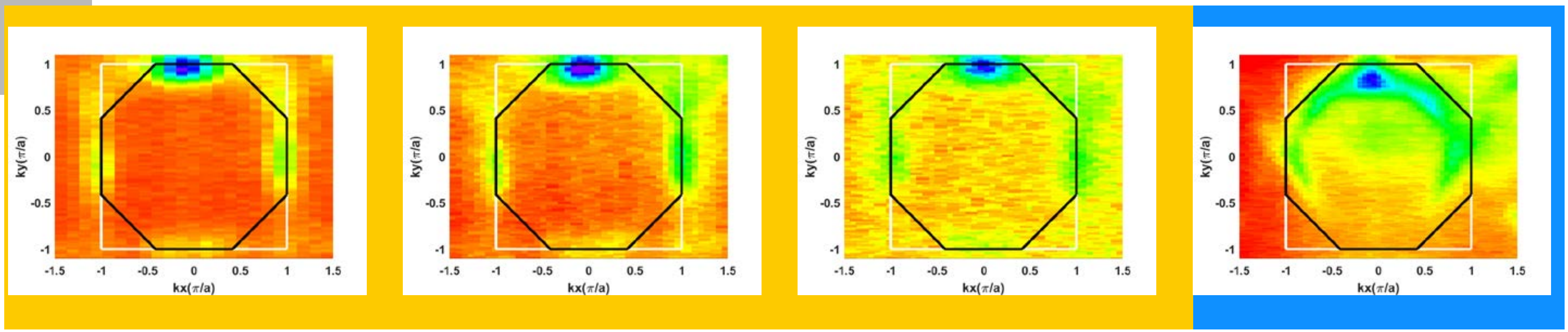



e.g.: Foyevtsova et al., PRB 91, 121114(R) (2015)

- Rice, Varma, *et al* in 80s: gap opened by attractive effective on-site interaction (-U)
- Not clear *a priori* whether we can trust single-electron calculations

# Doped BKBO

The evolution of constant energy map with doping up to superconductivity.




x=2% , E=-0.2eV

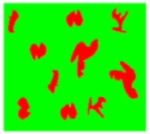
x=10% , E=-0.2eV

x=25% , E=-0.2eV

X=40%, E=Ef

$\delta = 0$

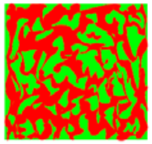
Insulator



$\delta_c > \delta > 0$

Percolative

Insulator



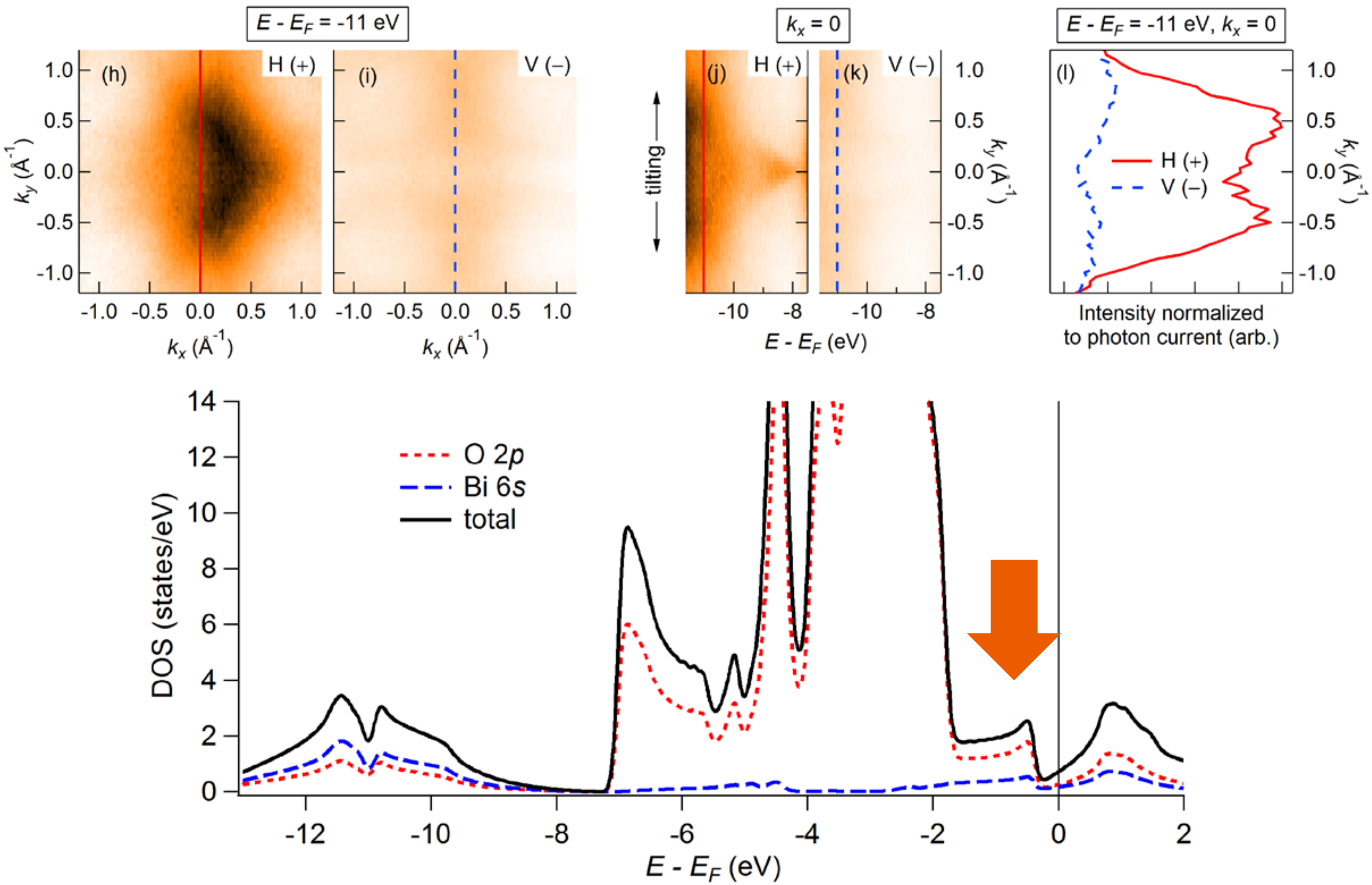
$\delta^* > \delta > \delta_c$

Percolative

Metal

Percolation picture from insulator to superconducting

# Polarization dependence

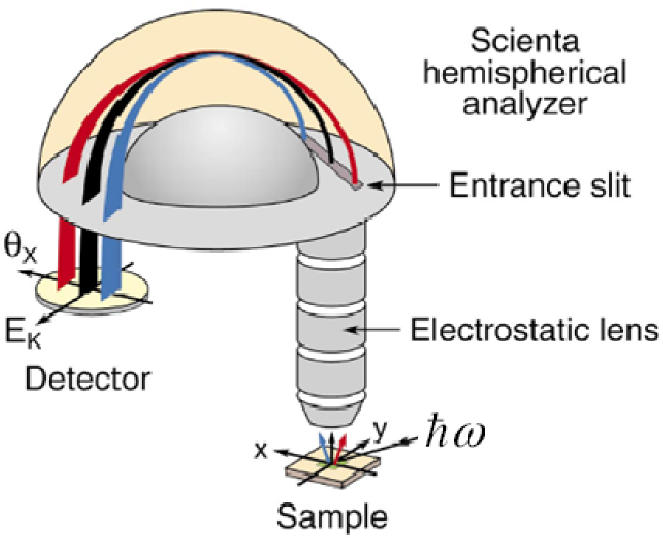


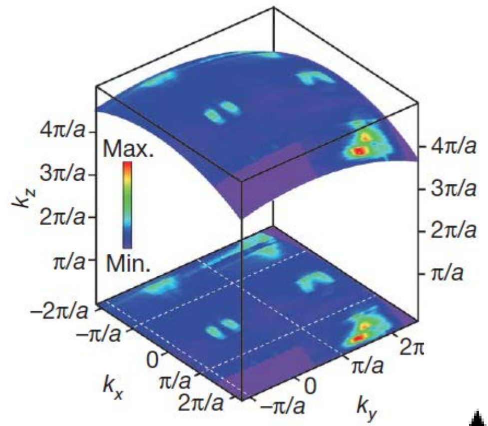

Plumb et al., PRL 117, 037002 (2016)

# Angle-resolved photoemission spectroscopy

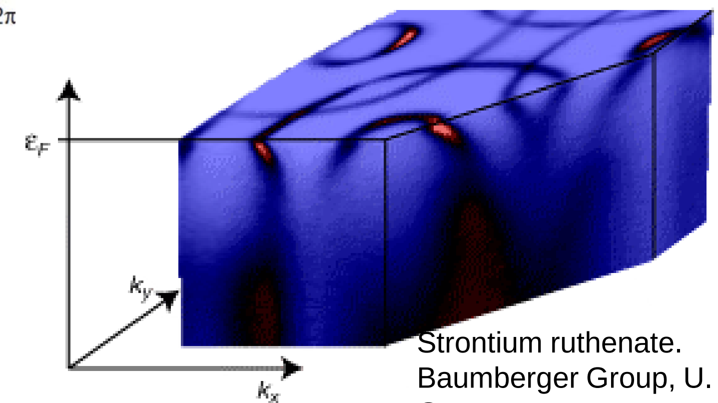
$$k_{\parallel} = K_{\parallel} = \frac{1}{\hbar}\sqrt{2mE_{kin}} \cdot \sin\vartheta$$

$$k_{\perp} = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\vartheta + V_0)}.$$




STO.
Nature **469**, 189 (2011).



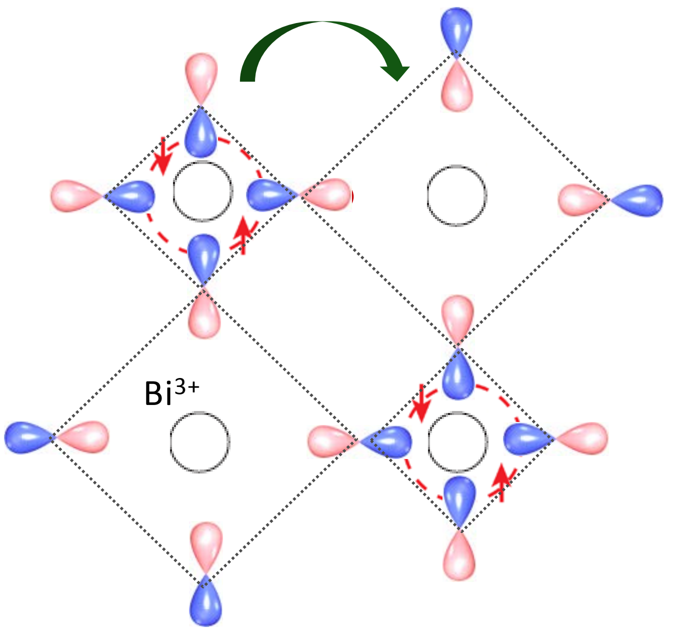

Strontium ruthenate.
Baumberger Group, U. Geneva

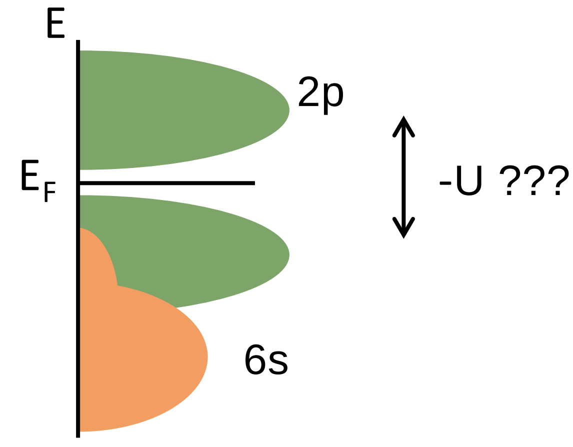
ARPES can map electronic structure in 4 dimensions

$(E, k_x, k_y, k_z)$

Review: Damascelli,Physica Scripta **T109**, 61-74 (2004).

# Half filled bi-polarons




- Polarons cannot move independently when there lattice distortions overlap.

# Weak electronic correlations

- LDA methods successfully compute most aspects of the band structure of BaBiO3.
- The electron correlations are weak.

zero-, single-, bi-polaron state