

# Local Ordering of Oxygen in High-Tc Superconductors (IS360)

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→ The  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  materials and their doping questions.

→ Experimental method

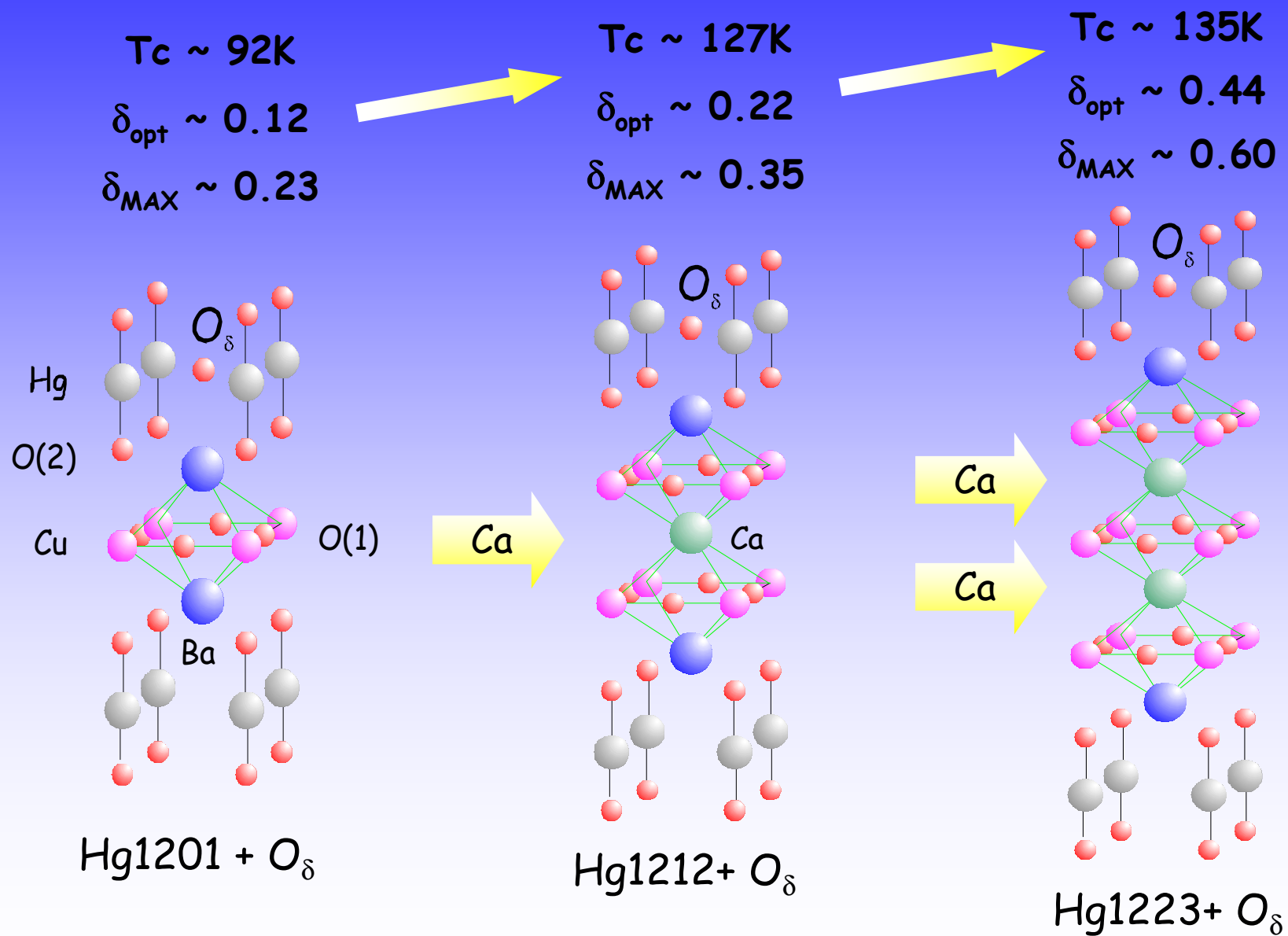
- $^{199\text{m}}\text{Hg}$  Perturbed Angular Correlation (PAC) experiments

→ PAC preliminary results in Hg-1212 and Hg-1223, influence of:

- annealing atmosphere: Argon and Oxygen pressure
- measurement temperature

→ Conclusions

# Hg-based Superconductors: $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$

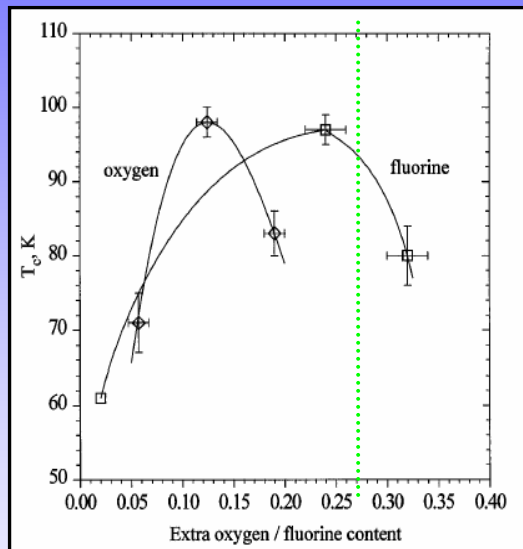


# Hg-1212 and Hg-1223 questions

How does occur charge transfer in  $\text{CuO}_2$  planes?

## Comparing dopant and doping effects

PRL80 (1998) 385



$$T_c = T_{c_{\max}} [1 - q(\delta - \delta_{\text{opt}})^2]$$

*Physica C* 176 (1991) 95

Ionic model: holes<sub>opt</sub> = 0.16

$\delta_{\text{opt}}(\text{O}) \sim 0.8$ ,  $\delta_{\text{opt}}(\text{F}) \sim 0.16$

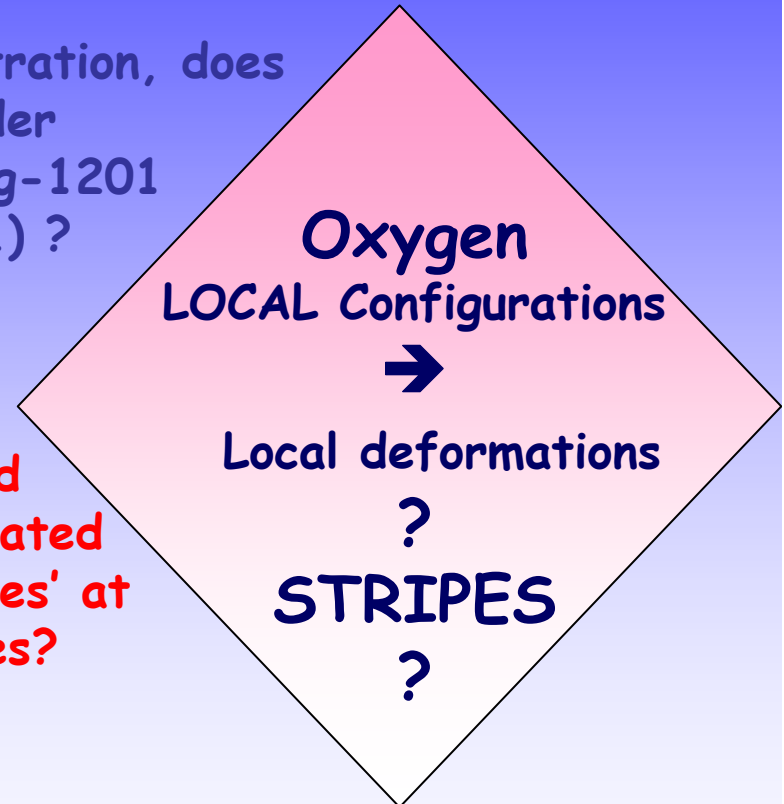
for high  $\text{O}^{2-}$  concentration, does oxygen order (as for  $\text{F}^-$  in Hg-1201 PRB 72(2005)1) ?



are order and deformations related with 'charge stripes' at the  $\text{CuO}_2$  planes?

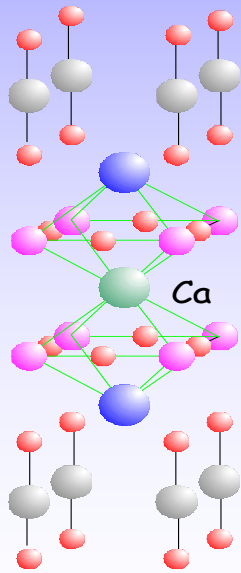
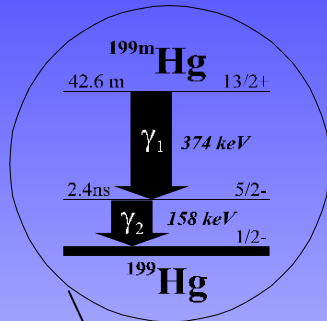


what happens with ordering below and above  $T_c$ ?



# Perturbed Angular Correlations PAC

Probe doping at ISOLDE/CERN  
 $^{199m}\text{Hg}$  implanted



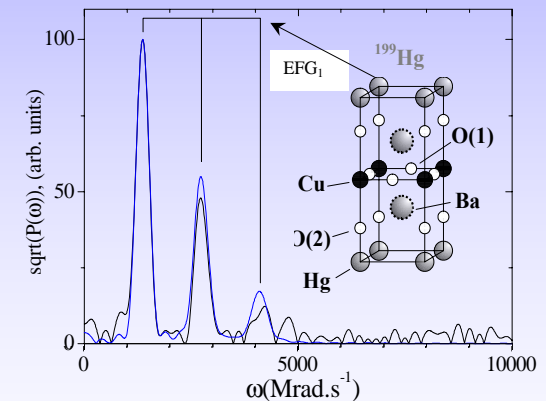
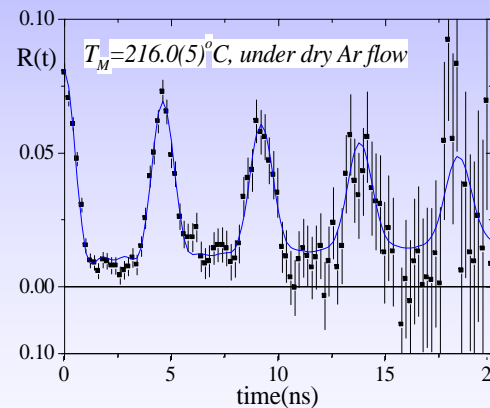
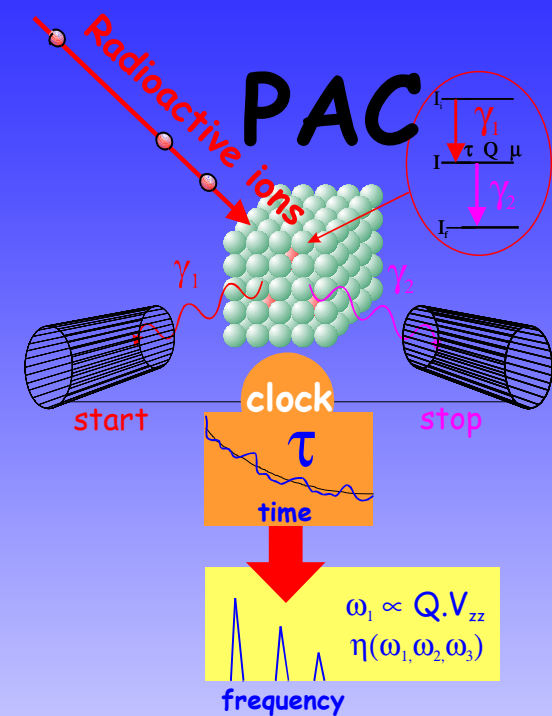
Hg1212+  $\text{O}_\delta$

Electric Field Gradient (EFG)

$$V_{zz}, \eta = (V_{xx} - V_{yy}) / V_{zz}$$



dopant configuration fingerprint



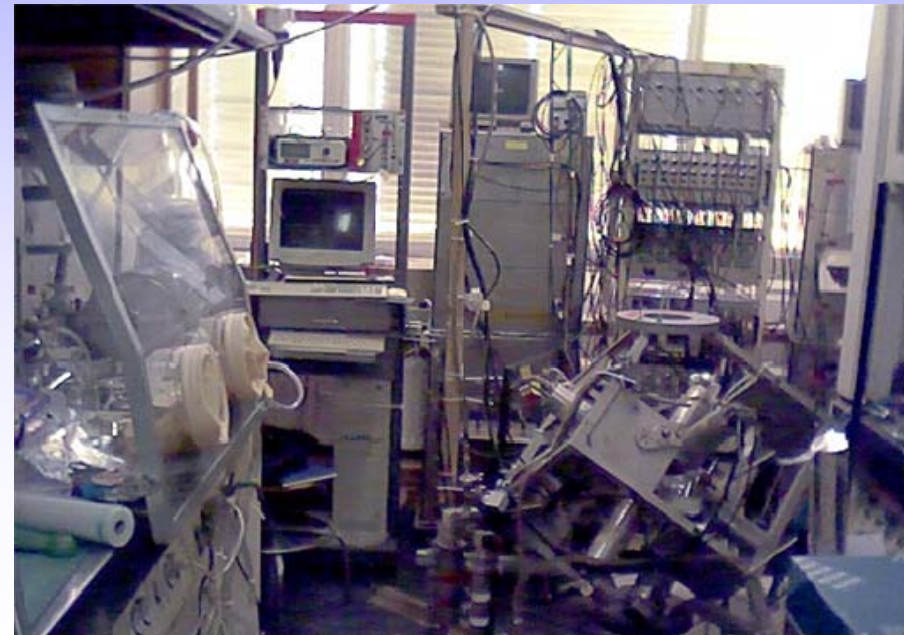
## Simulations:

Full-potential-linearized-augmented-plane-wave (FLAPW)

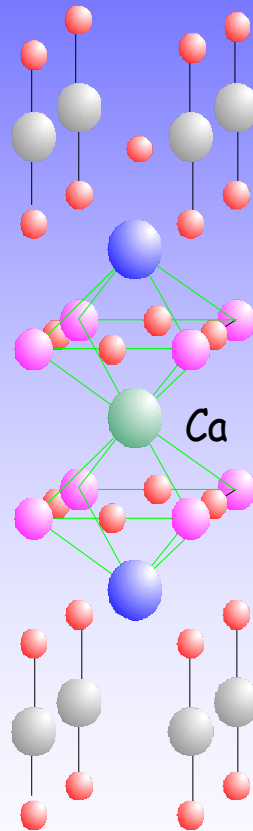
Electronic Structure Method

Local-density-approximation (LDA)

- ⇒ pellets of Hg1212 and Hg1223
- ⇒ vacuum implantation and transport
- ⇒ Manipulation: glove boxes under controlled atmosphere
- ⇒ Hg1212, Hg1223: Argon flow & oxygen pressure annealings
- ⇒ **PAC measurements, analysis/simulations**  
**(275/R-004, R-011)**



# Experiments with Hg-1212





# Oxygen doping in Hg-1212

TM= room temperature (RT)

⇒ 1<sup>st</sup> step annealing under Argon, 20 min, 190(10)°C

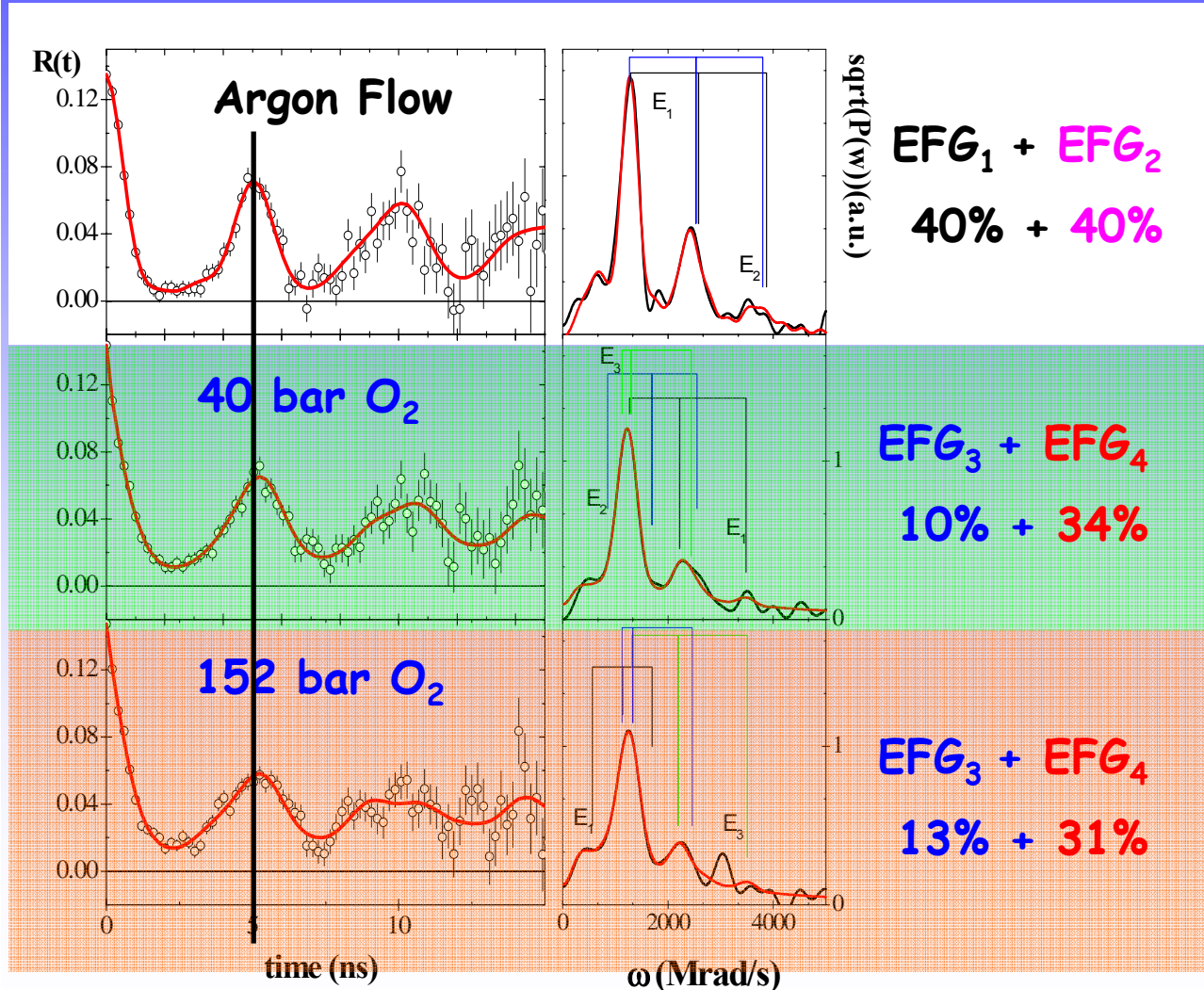
⇒ 2<sup>nd</sup> step annealing under pressurized O<sub>2</sub> (40 and 152 bar), 25 min.

fraction of probe Hg  
out of regular  
structural positions  
(attenuation in R(t)  
spectrum)

20%

56%

56%





# Preliminary results in high oxygen doping in Hg-1212

## Experiments

### Argon Flow

$f_1=40\%$ ,  $\eta_1=0$ ,  
 $\omega_1=1291.34$  Mrad/s

$f_2=40\%$ ,  $\eta_2=0.23$ ,  
 $\omega_2=1194.45$  Mrad/s

### 40 bar Oxygen

$f_3=10\%$ ,  $\eta_3=0.34$ ,  
 $\omega_3=1133.37$  Mrad/s

$f_4=34\%$ ,  $\eta_4=0.8$ ,  
 $\omega_4=720.53$  Mrad/s

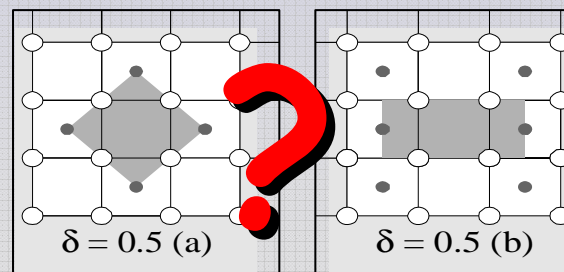
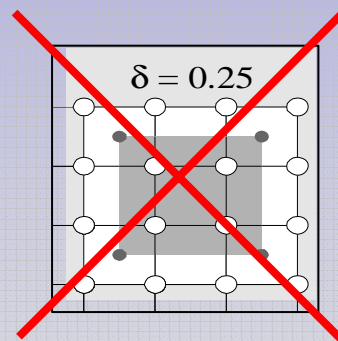
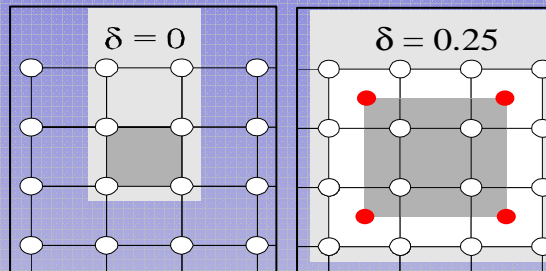
### 152 bar Oxygen

$f_3=13\%$ ,  $\eta_3=0.40$ ,  
 $\omega_3=1130.66$  Mrad/s

$f_4=31\%$ ,  $\eta_4=0.8$ ,  
 $\omega_4=731.18$  Mrad/s

## EFG simulations

(Hg-1201 doped with F)



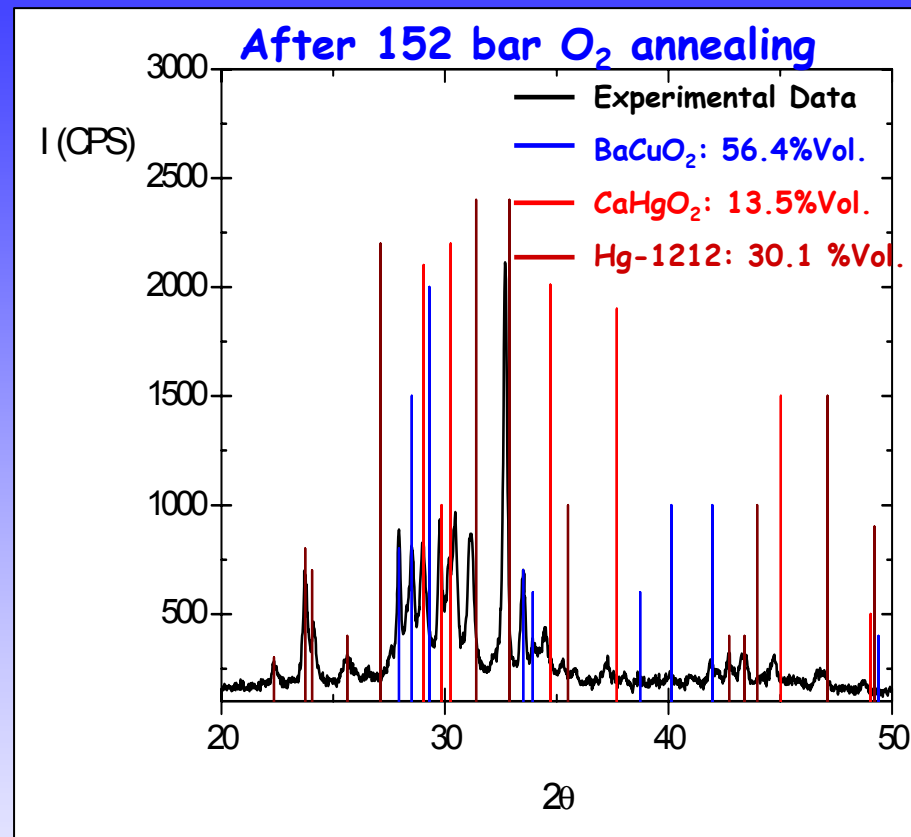
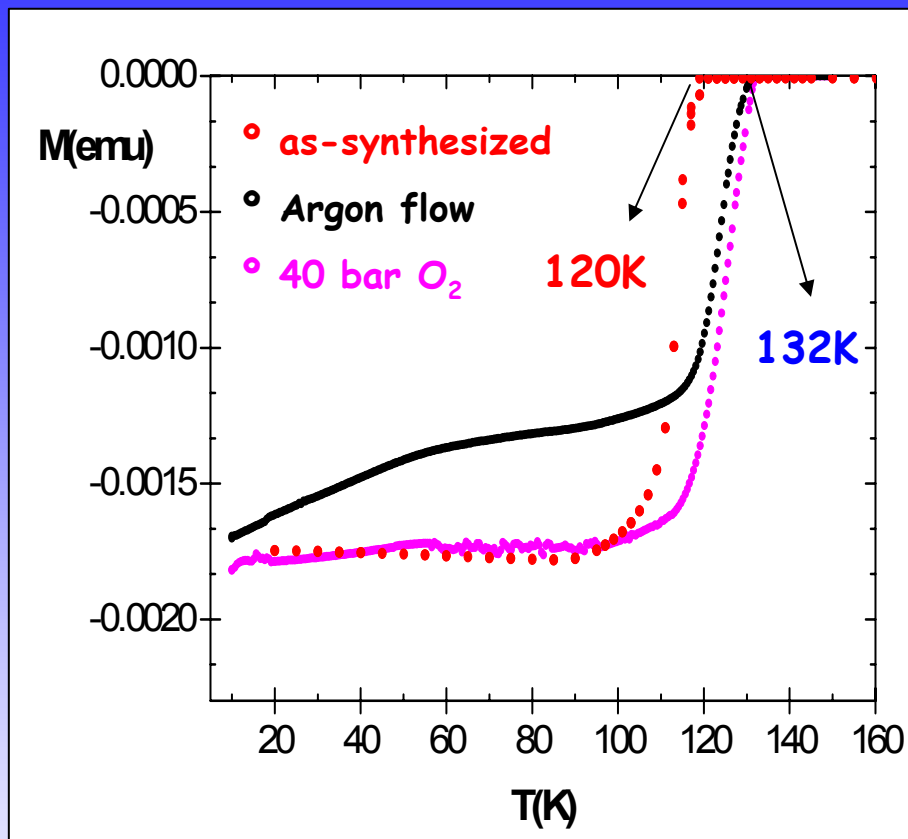
Local Hg  
environment with  
diluted oxygen  
concentration.

Axial EFG assymetry  
parameter very high

Local Hg environment  
with High oxygen  
concentration

Configurations under  
analysis

# Magnetic and XRD characterization of Hg-1212 samples

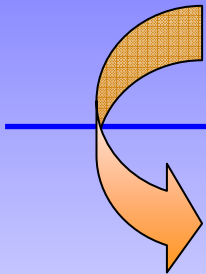


- Increase of  $T_{c,onset}$  after annealings from 120K to 132K
- Lost of superconductivity after 152 bar annealing

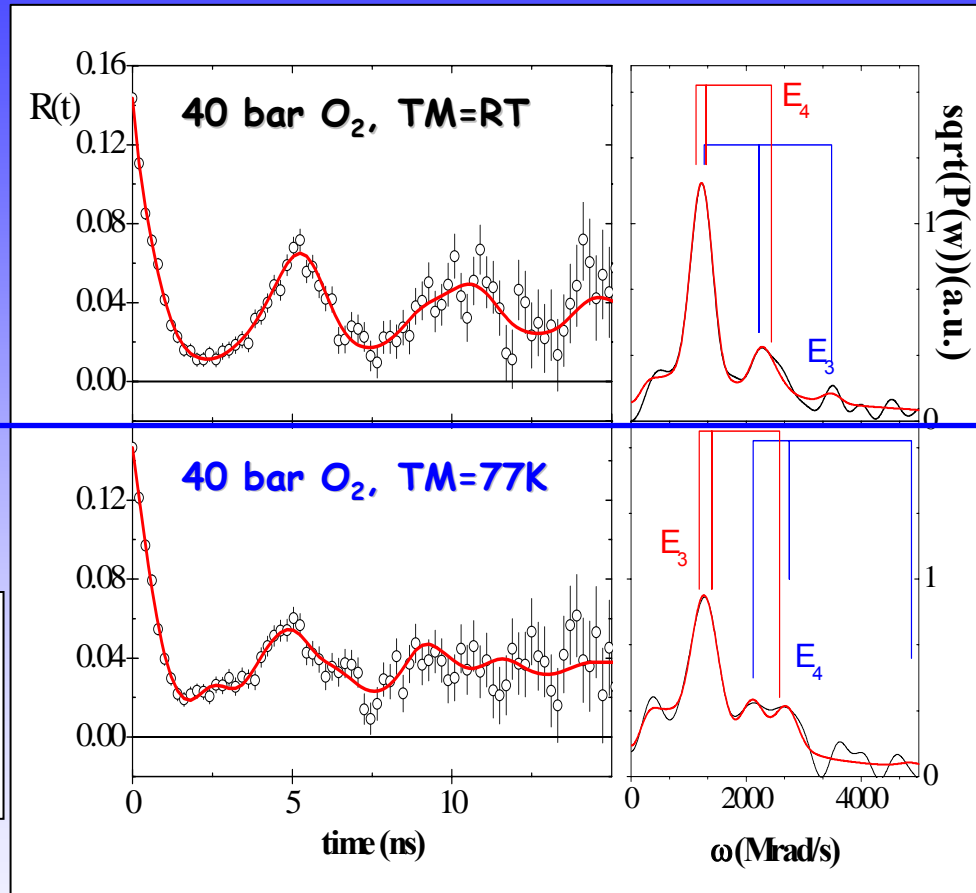
Decomposition of superconducting crystalline phase at 152 bar oxygen pressure in agreement with the attenuated fraction measured by PAC!

# High oxygen doping in Hg-1212: -What happens below $T_c$ ?

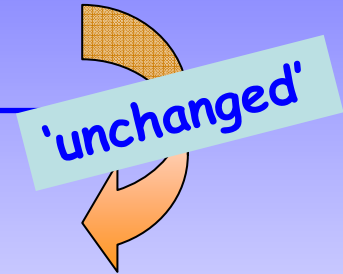
$f_3=10\%$   
 $\eta_3=0.339$   
 $\omega_3=1133.37$  Mrad/s



$f'_3=16\%$   
 $\eta'_3=0.696$   
 $\omega'_3=1483.25$  Mrad/s

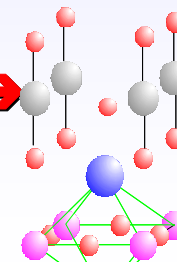


$f_4=34\%$   
 $\eta_4=0.820$   
 $\omega_4=720.53$  Mrad/s

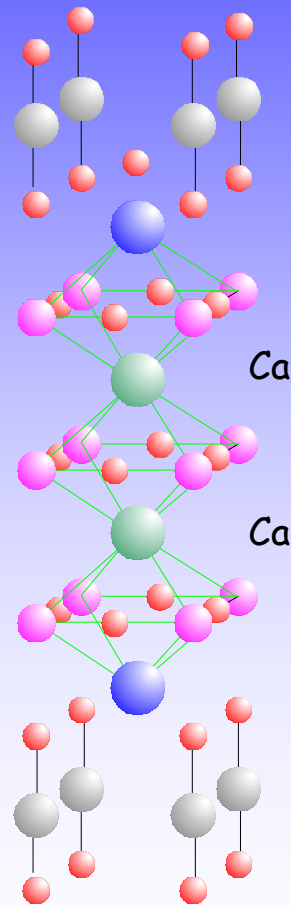


$f_4=31\%$   
 $\eta_4=0.800$   
 $\omega_4=768.61$  Mrad/s

...at low temperature, below  $T_c$   
 there are oxygen,  $O_\delta$ , rearrangements  $\rightarrow$

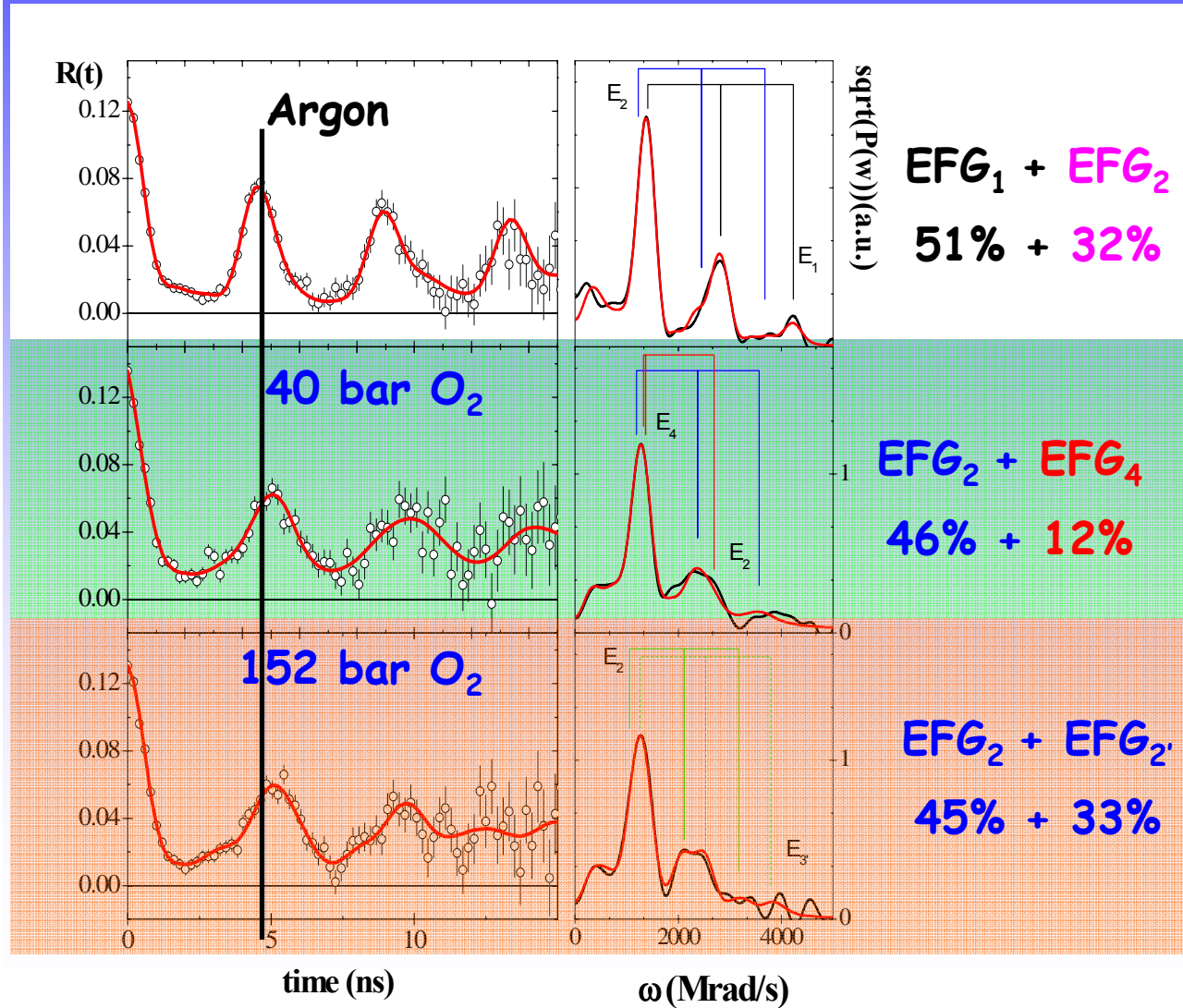


# Experiments with Hg-1223



# Oxygen doping in Hg-1223 $T_M$ = room temperature (RT)

- ⇒ 1<sup>st</sup> step annealing under Argon 20 minutes, at 190(10)°C
- ⇒ 2<sup>nd</sup> step annealing under pressurized O<sub>2</sub> (40 and 152 bar), 25 min.



17-43%: fraction of probe atoms not in regular position - attenuation in R(t) spectrum!

17%

42%

22%

# Preliminary results in high oxygen doping in Hg-1223

## Experiments

### Argon Flow

$f_1=51\%$ ,  $\eta_1=0$ ,  
 $\omega_1=1409.97$  Mrad/s

$f_2=32\%$ ,  $\eta_2=0.15$ ,  
 $\omega_2=1233.66$  Mrad/s

### 40 bar Oxygen

$f_2=46\%$ ,  $\eta_2=0.17$ ,  
 $\omega_2=1189.25$  Mrad/s

$f_4=12\%$ ,  $\eta_4=0.9$ ,  
 $\omega_4=770.59$  Mrad/s

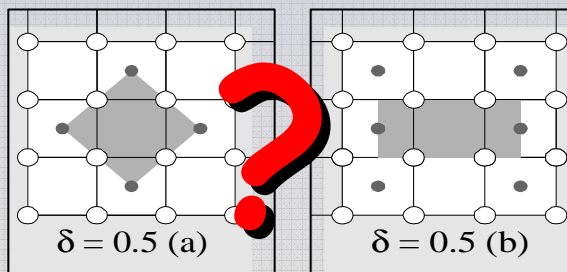
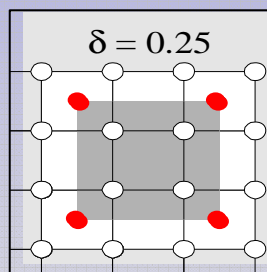
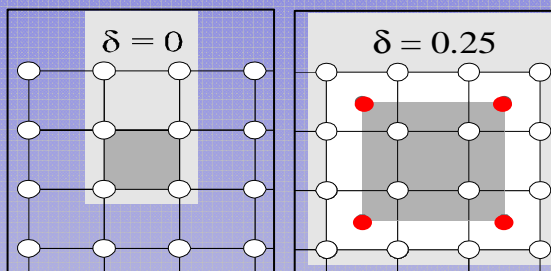
### 152 bar Oxygen

$f_2=44\%$ ,  $\eta_2=0.26$ ,  
 $\omega_2=1265.5$  Mrad/s

$f_2=34\%$ ,  $\eta_2=0.3$ ,  
 $\omega_2=1058.38$  Mrad/s

## EFG simulations

(Hg-1201 doped with F)



Local Hg environment with diluted oxygen concentration.

$f_2$ : Local Hg environment with one oxygen atom at the centre of the Hg mesh

$f_4$ : Axial EFG assymetry parameter very high for 40 bar

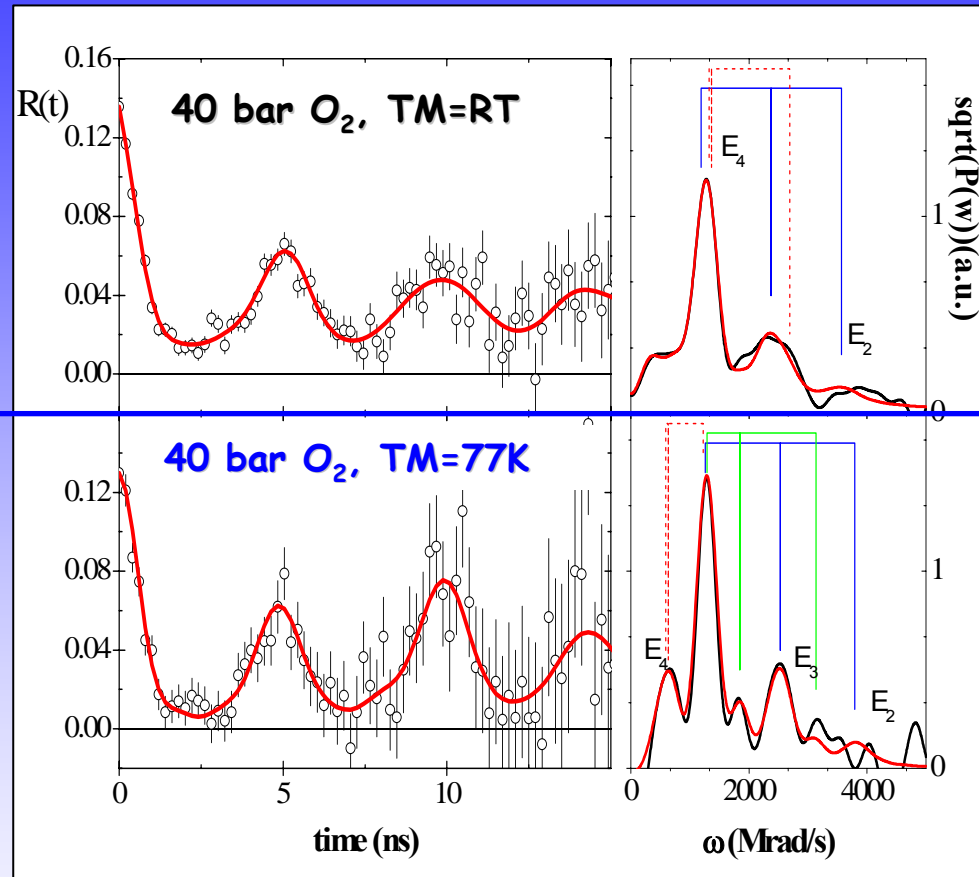
Configurations under analysis

# High oxygen doping in Hg-1223: - what happens below $T_c$ ?

$f_2=46\%$   
 $\eta_2=0.172$   
 $\omega_2=1189.25$  Mrad/s

'unchanged'

$f_2=58\%$   
 $\eta_2=0.178$   
 $\omega_2=1253.43$  Mrad/s



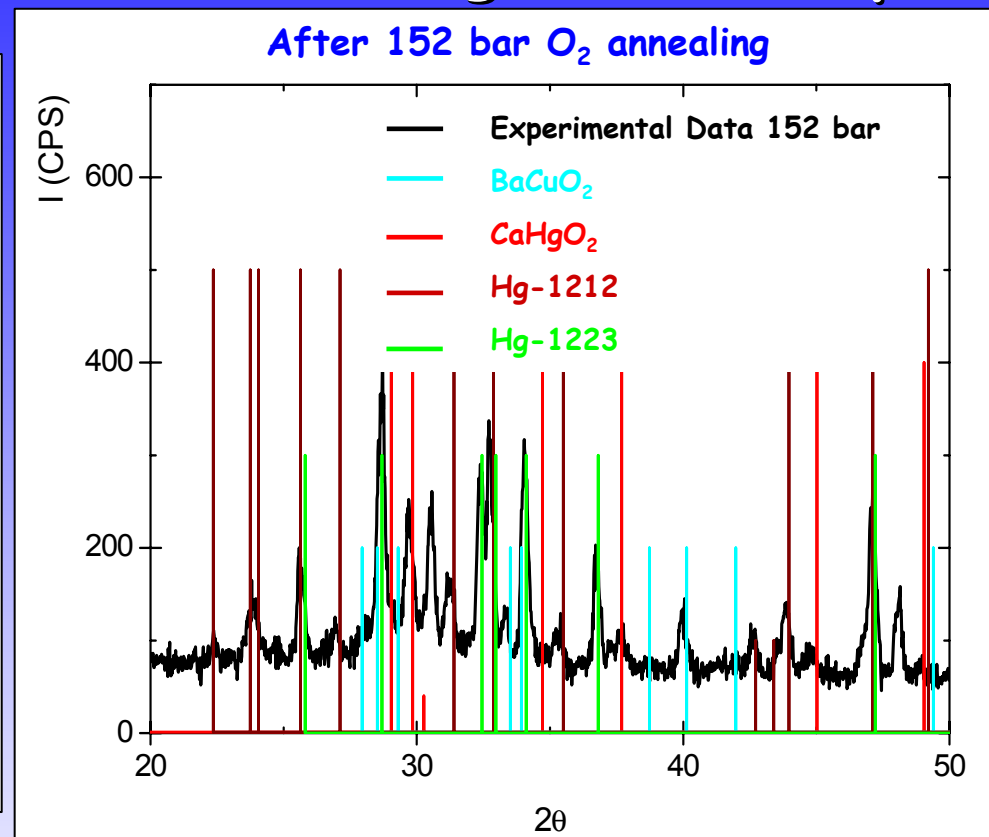
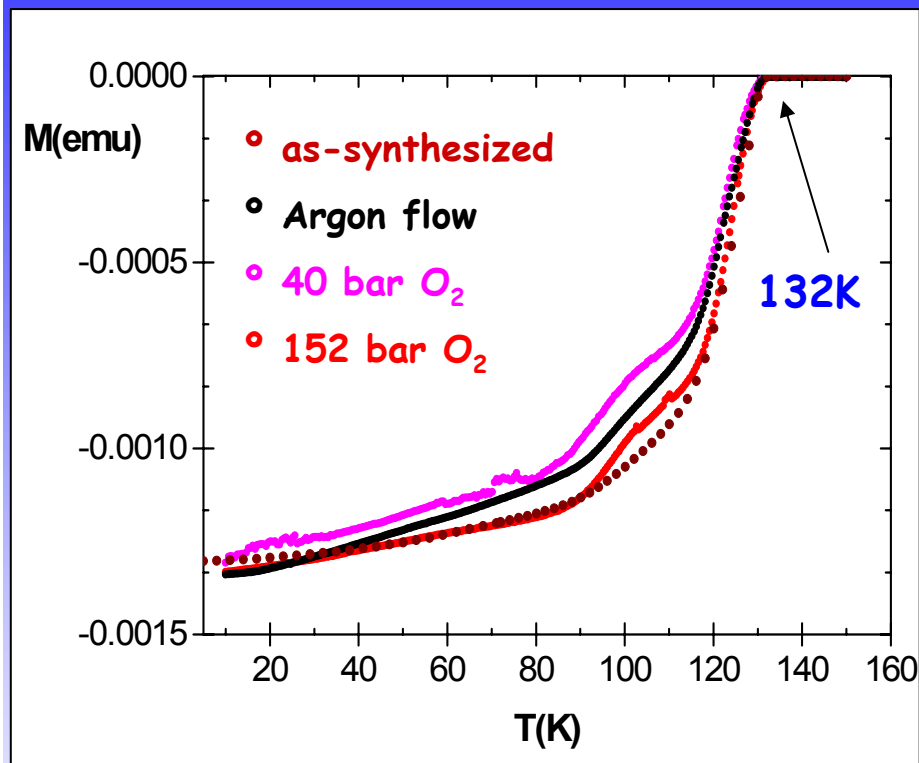
$f_4=12\%$   
 $\eta_4=0.960$   
 $\omega_4=770.59$  Mrad/s

$f_3=19\%$   
 $\eta_3=0.300$   
 $\omega_3=1064.02$  Mrad/s

Oxygen, O<sub>δ</sub>, configuration rearrangements: YES  
 Hint: differences between Hg-1223 and Hg-1212  
 are due to different O<sub>δ</sub> concentrations.



# Magnetic and XRD characterization of Hg-1223 samples

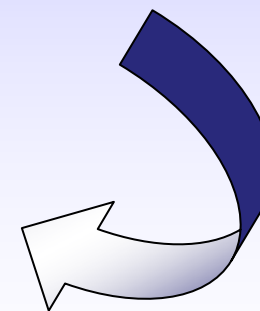


- No changes in  $T_{c,onset}$
- Different transition shapes due to inhomogeneous in-bulk oxygen doping

Hg-1223 (%Vol.)

40 bar: 66.4%

152 bar: 59.5%



# Summary

## Oxygen doping in Hg-1212 and Hg-1223

Ar annealing → diluted oxygen concentration in the probing zone.

**O<sub>2</sub> pressure annealing** → Strong non- axially symmetric local charge distributions (maximum  $\eta=0.9$ , configurations under analysis).

PAC measurements below T<sub>c</sub> hint rearrangements of the local Hg environment in the oxygen doped samples probably dependent of local oxygen concentration (to be further investigated).

In Hg-1212 samples, there was lost of superconductivity for the annealings at 152 bar as showed by the magnetic measurements, probably overdoping - X-ray under analysis

To finish this work we need:

A systematic study of cell parameters ( $a$ ,  $c$ ) to infer bulk sample O $\delta$  doping (in progress from XRD data)

Study of EFG simulations looking forward to identify the found local oxygen configurations.

**Thanks!**

# Collaborations



# Work Organization

