

# Theory/experiments of X-Ray flux effect on periodic lattice distortions in YBCO<sub>7-δ</sub>

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## ABSTRACT

The effect of X-ray flux on periodic lattice distortion waves in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>, YBCO<sub>7-δ</sub> 50nm films, on SrTiO<sub>3</sub>, is described: The flux  $r(t)=d[\text{photons}]/dt$  induces resonant excitations:  $h\nu+YBa_2Cu_3O_{7-\delta} \rightarrow X^z$  that indicate a path for the transition:  $YBCO_{7,\text{metal}} \leftrightarrow X^z \leftrightarrow YBCO_{6.5,\text{insulator}}$ . The mole fraction,  $y_{YBCOx}$  at  $r(t)$  (determined by inserting Al filters  $t$  mil thick) obeys the relation:  $1/y_{YBCO} = 1 + r(t) T_1$  (fig. 1) where  $T_1$  is the  $X^z$  lifetime and  $1/T_1$  is of order  $r(t) \sim 10^{10}/s$  achieved in synchrotrons. **Figure 1:** 1-12 XRD at 8.048keV,  $\Omega=0$ , 298K versus  $\phi-\phi_0$  at different incident photon rates,  $r(t)$ . Insert shows the experimental fit  $1/y_{YBCO} = S(\infty)/S(t)$  versus  $r(t)/r(t_0)$  to obtain  $T_{1,(1-12)} = 0.4/r(t_0)$ .

**Keywords:** Nano-particle SCF calculation, periodic lattice distortions, nano-film synchrotron radiation XAS and XRD.

## 1. INTRODUCTION

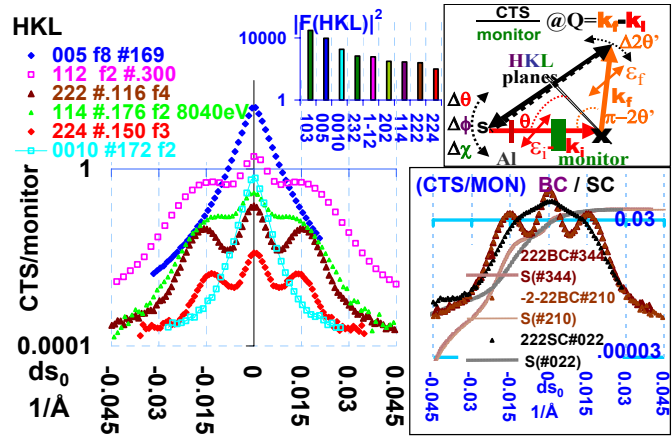
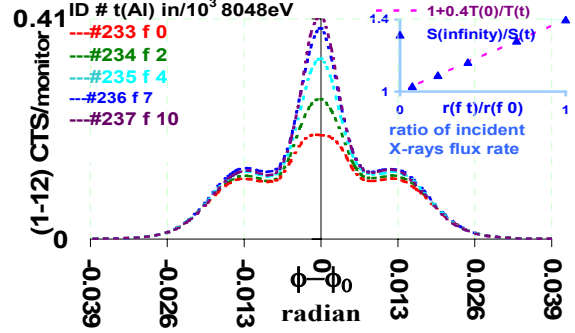
A study of YBCO nano films, important for industrial applications, compares phenomena in films to bulk crystals.

## 2. EXPERIMENTAL

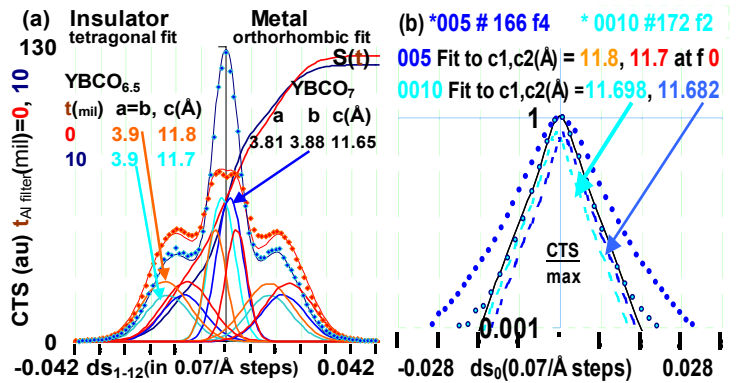
50 nm YBCO epitaxial films, grown by sputtering in an oxygen atmosphere on a SrTiO<sub>3</sub>, STO 100 plane, with and without a 24DEG ab grain boundary, GB at the Complutense University<sup>[1a,b]</sup> were characterized by plane polarized synchrotron photon energy 7 to 9.5keV XRD at SSRL-7-2 at 298K (fig. 1-3) and by 001 enhanced scattering ( $I_s/I_0$ ) collected at LBNL-ALS-6.3.1 at 0.5 to 2 keV in the Kortright chamber at different temperatures<sup>[1c-e, 2]</sup> (fig. 4, 8) and distinguished from fluorescence ( $F/I_0$ ) and total electron yield ( $TEY/I_0$ ) in the Nachimuthu chamber<sup>[1c-e, 3]</sup>. E was calibrated at  $E(\text{CuO}, \text{Cu:L}_3) = 931.2\text{eV}$ <sup>[1d]</sup>. Samples are identified by the STO substrate single crystal, SC or two fused with a 24° ab GB, BC qualified by the year fabricated/year measured. The O composition is ascertained from bulk crystal XRD data<sup>[4,5]</sup>. The incident plane polarized beam  $\mathbf{I}_i = \{k_i, \varepsilon_i, h_i\}$  10 by 100μm wide, intensity  $I_0$ , on the 1cm<sup>2</sup> film at  $\mathbf{x}$  (fig. 2 insert) makes an angle  $\theta$  to the scattering plane and  $2\theta'$  to the scattered beam  $\mathbf{I}_f = \{k_f, \varepsilon_f, h_f\}$  detected versus  $\mathbf{s} = \{s_0, 0, 0\} + d\mathbf{s}$ ,  $s_0 = \sqrt{(H^2/a_0^2 + K^2/b_0^2 + L^2/c_0^2)} = 2\sin\theta_0/\lambda$  and the CTS/monitor record the intensity of the momentum transfer  $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i = s_0 \{-\cos(\theta' - \theta), \sin(\theta - \theta'), 0\}$ <sup>[4j]</sup> versus  $\theta, \chi, \phi$  (fig. 1-4). Then:

$$d\mathbf{s} = s_0 \{ \cot\theta, 1, 0 \} d\theta, s_0 \{ 0, 0, d\chi \}, \text{ and } s_0 \{ 0, \cos\chi, 0 \} d\phi \quad (1)$$

versus  $\Delta\theta, \Delta\phi$  with  $2\theta' = 2^* \theta_{\text{Bragg}}$ , and  $\Delta H = -\Delta K$  scans obtain H,K,L≠0 XRD with sidebands sb to the center-band cb (fig. 1-3),  $\phi_0 = \text{atan}(a_0 K/b_0 H) + C$ ,  $\chi_0 = \pi/2 + \text{acos}(L/c_0/s_0)$ . Inverse rotations obtain the orientation dependent amplitudes  $\varepsilon$



**Figure 2:** 298K YBCO BC04/04 50nm film XRD semi-log CTS per monitored incident beam intensity with Al filters  $t, t''/10^3$  thick versus  $ds_0 = 2(\sin\theta - \sin\theta_0)/\lambda$ ,  $E = 8.04\text{keV}$ . Inserts show:  $|F(\text{HKL})|^2$  for  $D^{17}_{2h}$  YBCO to identify the structure, the sample geometry, and the SC film superimposed on the resolved BC film 222 XRD-PLD.



**Figure 3:** XRD scans versus  $\theta$  fitted to two phases at 298K: (a) 1-12 XRD,  $t=0$  and 10 mil identify an unchanged orthorhombic phase plus a tetragonal ( $a=b, c$ )  $\rightarrow (3.89, 11.69\text{\AA})$  as  $t$  increases, equally abundant phases. (b) 0010 XRD Lorentzian line shapes ( $\text{HWHH} \approx 0.08 \text{ DEG}$ ) convoluted with a Gaussian ( $\text{HWHH} \approx 0.3 \text{ DEG}$ ) for the phases determined in (a). The  $sb_{\pm 1}$  maxima at  $q_x = \pm q_y \approx a^2 s_0 ds_{sb\pm 1} / 2H \approx 1/24$  (fig. 2, 3a), obtained the PLD vector<sup>1b,d1</sup>, agreeing with  $dK, -dH$  scans that determine the diagonal  $q_{xy} = (dK_0/K - dH_0/H)_{sb\pm 1} \approx 2^{-1/2}/24, H, K, L \neq 0$  (fig. 8).

along the a,b,c crystal axes, and project  $\mathbf{ds}$  into the reciprocal lattice axes<sup>[4i]</sup> that plot the rocking curves versus the respective abscissa (fig. 2-4). When  $\varepsilon=\varepsilon_i\approx\varepsilon_f$ ,  $\mathbf{k}=\mathbf{k}_i\approx\mathbf{k}_f$ ,  $\mathbf{I}_f=\{k_f\sin(2\theta'-\theta) - \varepsilon_f\cos(2\theta'-\theta)\}$ ,  $k_f\cos(2\theta'-\theta) + \varepsilon_f\sin(2\theta'-\theta)$ ,  $h_f\}$ .

The XRD integrated intensity  $S(t)$  at an incident X-ray flux  $r(t)$  is proportional to the mole fraction of a given  $\text{YBCO}_x$  phase detected at  $\Omega=2\theta'-2*\theta_{\text{Bragg}}=0$  for the given HKL (fig. 1). The rate of incident photons  $r(t) = d[h\nu]/dt = r(f_0)T(0)/T(t)$ ,  $r(f_0)\approx 10^{10}\text{s}^{-1}$  is decreased by inserting Al filters  $f_t$ ,  $t$  mil thick in the path of  $\mathbf{I}_i$ , (fig. 2) and counting for a time  $T(t)$  to achieve constant monitor counts versus  $t$ .

## DISCUSSION OF RESULTS

The data analysis is based on the structure factor<sup>[4, 6a]</sup>:

$$F=\sum_j f_j(\mathbf{k}_i, \mathbf{k}_f, E)=\sum_j[\alpha_j f_j^o(\mathbf{k}_i, \mathbf{k}_f)+\Delta f_j(\mathbf{k}_i, \mathbf{k}_f, \varepsilon_i, \varepsilon_f, E)]. \quad (2)$$

$f_j^o$  leads to Bragg scattering, resonance effects are due to:  $\Delta f_j\propto\sum_n\langle\varepsilon_f\mu_{in}e^{-i\mathbf{k}_f\cdot\mathbf{r}_j}\rangle\langle e^{i\mathbf{k}_i\cdot\mathbf{r}_j}\mu_{ni}\varepsilon_i\rangle/[(E_n-E_i-h\nu_{in}+\Delta_n)-i\text{HWHH}]$  plus its Hermitian conjugate,  $\mu_{in}$  is the dipole matrix element between initial and final excited states  $n, l$  with energies  $E_n, E_l$ , the state lifetimes determine the half width at half height HWHH,  $\alpha_j = \sum_i \exp(i(\mathbf{k}_i-\mathbf{k}_f)\cdot\mathbf{r}_j)$  are the crystallographic site weights,  $\Delta_n = \text{Lamb shift}$ . The relative sb to cb scattering intensity when a PLD displaces an atom  $l$  at  $\mathbf{R}_{0l}$  to  $\mathbf{R}_f=\mathbf{R}_{0l}+\delta_l$  when  $\delta_l=\mathbf{u}_i \exp(i(2\pi\mathbf{R}_{0l}\cdot\mathbf{q}+\phi))$ <sup>[1b,d,4a,g]</sup>.

$$\text{Area}_{\text{side-band, } n=\pm 1} / \text{Area}_{\text{center band}} = |J_1(z_l)/J_0(z_l)|^2, \quad (3)$$

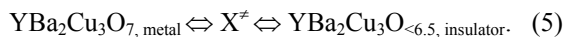
is non-zero when  $(\mathbf{s}+\mathbf{nq})\cdot(\mathbf{R}_f-\mathbf{R}_{l-1})$  and  $n$  are integers,  $z_l=2\pi\mathbf{u}_i\cdot\mathbf{s}$  and  $J_n$  are ordinary Bessel functions (fig.1-3). H $\pm$ HL XRD-PLD obtain  $\mathbf{q}\approx\pm(1,-1,-0)/24$ ,  $\mathbf{u}\geq 0.04$  (a,-b,-0) (fig. 2) that describes YBCO twin formation where the angles  $\mathbf{b}\wedge\mathbf{a}=90^\circ\pm 0.02\%$  and  $\text{atan}(b/a)=45.05^\circ\pm 0.12\%$  remain constant along one plane diagonal forming stripes as shown below (fig. 5, 6). The SC film 222 XRD superimposes on the BC sideband structure (fig.2 insert) where the integral  $S$  shows inflection points at  $ds_0=-0.30/\text{\AA}$  for  $sb_{-2}$  suggests that PLD are present also on SC but resolved only in BC films.

Important evidence for the rate of exchange between at least two phases is obtained as follows: **i.** The dependence of HKL scattered intensity  $S(t)$  versus the incident X-ray flux at 8.048keV indicates that resonance excitations to an activated complex  $X^\ddagger$  (fig. 1) determines the detected YBCO mole fraction at  $\Omega=2\theta'-2*\theta_{\text{Bragg}}=0$ :  $y_{\text{YBCO}}=S(t)/S(\infty)$ , and at steady state obtains:

$$-dy_{\text{YBCO}}/dt = r(t) y_{\text{YBCO}} = dy_{\text{YBCO}}/dt = (1-y_{\text{YBCO}})/T_1,$$

$$1/y_{\text{YBCO}} = S(\infty)/S(t) = 1 + T_1 r(t) \quad (4)$$

where  $1/T_1(005)=0.2r(f_0)$  is slower than  $1/T_1(1-12)=2.5r(f_0)$  (fig.1), and  $|F(005)/F(1-12)|\approx 10$  suggests that the  $X^\ddagger$  lifetime  $T_1$  depends on  $E, \varepsilon$  and the total scattering cross section, and therefore may be due to resonance transitions near 8040 to 8048eV (eq. 2). Then  $1/T_1$  is equal to the sum of the Einstein induced and spontaneous emission rates that leads to a steady state equilibrium:



where  $\Delta E_{n1}^{-1}|\mu_{n1}\varepsilon_{1-12}|^2/\Delta E_{n1}^{-1}|\mu_{n1}\varepsilon_{005}|^2\approx 10$  are the relative transition probabilities due to resonance effects<sup>[6c]</sup> and,

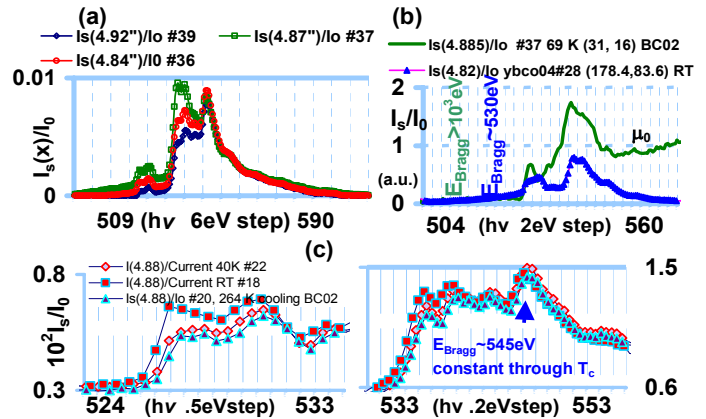
$$\{\varepsilon_a^2+\varepsilon_b^2, \varepsilon_c^2\}/\varepsilon^2 = \{0.8, 0.2\}_{1-12, 8048\text{eV}}; \{0.1, 0.9\}_{005, 8040\text{eV}},$$

but these were not observed at 7, 8 or 9.5keV. **ii.** The 1-12  $sb_{\pm 1}$  and 0010, 005 XRD (fig. 3) may be fitted to at least two phases with a Lorentzian line shape, with  $(\text{HWHH})_L\leq 0.1\text{DEG}$ , convoluted in order to fit the wings with a Gaussian,  $(\text{HWHH})_G\approx 0.4\text{DEG}$  that indicates a broadening of  $2\pi\text{s}$  by  $\Delta k=4\pi(\text{HWHH})_G/\lambda_{\text{c}}\approx 0.04/\text{\AA}$  due to a dynamic exchange rate  $\omega\approx (k_B T/m_0)^{1/2}\Delta k\geq 10^{10}\text{s}^{-1}\approx 1/T_1$  (for  $m_0=0$  atomic mass) as described in liquids<sup>[4c]</sup>. Thus  $X^\ddagger$  at 298K is an intermediate between at least two equally abundant metal and insulator phases enhanced by X-ray resonance effects in the soft YBCO film, but may also be an intermediate in other phase transitions, e.g., versus  $T$ .

Enhanced scattering  $I_s/I_0$  was used to determine that more than one phase is present in the film<sup>[1d]</sup>. Hanzen<sup>[5a]</sup> has correlated the O composition in  $\text{YBCO}_{7-8}$  with the unit cell  $c_i$ . Energy shifts in the 001  $I_s/I_0$  enhanced peak (fig. 4, at fixed  $\theta, 2\theta'$ ) indicate the presence of different  $c_i$  phases as the incident beam scans the film surface near a GB. Here:

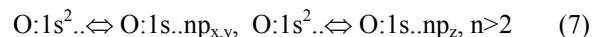
$$\Delta c_i/c_i\approx -\Delta E_{\text{Bragg}}/E_{\text{Bragg}} \quad (6)$$

follows from the 001 Bragg relation, and  $E_{\text{Bragg}}>E(\text{O}_{K\text{-edge}})$  obtains  $f^0$  as a baseline correction leading to  $I_s/I_0$  (eq. 2, fig. 4) similar to the  $\text{O}_{K\text{-edge}}$  XAS<sup>[1d, 6c, 7]</sup>. Farther than 100  $\mu\text{m}$  from the GB, a peak at  $E_{\text{Bragg}}=545\text{eV}$  obtains  $c_i=11.7\text{\AA}$  for the ortho-I  $\text{YBCO}_{-6,9}$ , but the growth of a new enhancement peak within 100 $\mu\text{m}$  of the GB, at  $\sim 540\text{eV}$  indicates in addition the presence of a higher  $c_i, \text{GB}\approx 11.8\text{\AA}$  for  $\text{YBCO}_{\leq 6.5}$ . The 8% O composition decrease in this phase may be due to flux heating and dynamic plastic interfacial strain<sup>[4c,d,m 5d,e]</sup>.



**Figure 4:** Enhanced 001  $I_s/I_0$  scattering near the O:K edge for BC02/03, BC04/04: **(a)** At different beam position  $\mathbf{x}$  near the GB. **(b)** For different values of  $E_{\text{Bragg}}$  normalized to XAFS:  $\mu_0 = 1 = \alpha_{O-1}$ . **(c)** Constant  $I_s/I_0$  peak observed at  $E_{\text{Bragg}} = 545 \text{ eV}$  indicates there is no  $c_i$  change through  $T_c$ .

001  $I_s/I_0$  at different  $E_{\text{Bragg}}=E(\text{O}_{K\text{-edge}})+\text{DE}$  correlate with the bulk XAS<sup>[5a,6c]</sup>(fig. 4), but in addition since (2) depends on the crystallographic weights  $\alpha(\mathbf{k}_i-\mathbf{k}_f)$  (Table I) the transition:



changes in  $I_s/I_0$  from  $DE=0$  to  $1500\text{eV}$  identify the O:i site edges by the changes in  $\alpha(\text{O:i})$ : **i.** The O:2 edge is near  $528-\delta$  by the doubling of  $\alpha(\text{O:2})$ . **ii.** The O:1 edge is near  $528+\delta$  to  $530\text{eV}$  by the constant intensity as  $\alpha(\text{O:2})/\alpha(\text{O:1}) = 0.8, 1.9$  sharpening below  $T_c$  and. **iii.** The O:3<sub>A,B</sub> edge is near  $531-535\text{eV}$  by the sign changes in  $\alpha(\text{O:3}_{A,B})$  vs DE:

$I_s/I_0(\alpha(\text{O:3}_{A,B}, DE=1.5\text{keV}) \approx 3.2) > 0$ ,  $I_s/I_0(\alpha(\text{O:3}_{A,B}, DE=0) \approx 2.8) \leq 0$ . These assignments, obtained earlier by XAS and XPE<sup>[6c, 7]</sup> in the bulk crystal indicate that the O atoms electro-negativity/shielding varies in the YBCO lattice: If the O:1 and O:2 sites are occupied by  $\text{O}^{2-}$  ions then O:3<sub>A,B</sub> are occupied by  $\text{O}^{-(0 \text{ to} \leq 1)}$  and  $\text{CuO}_2$  is a covalent conduction layer as graphite. Also, since the effect of X-ray flux depends on HKL where  $|\sum f_{\text{O}} \alpha_{\text{O:3}_{A,B}}|/|\sum f_{\text{Cu}} \alpha_{\text{Cu}2}|_{\text{HKL}=\text{005}} \approx 2$ ,  $|\sum f_{\text{O}} \alpha_{\text{O:3}_{A,B}}|/|\sum f_{\text{Cu}} \alpha_{\text{Cu}2}|_{\text{HKL}=\text{112}} \approx 0.1$  correlate with  $T_{1,005}/T_{1,112} \approx 10$ , this suggests that  $X^\pm$  is produced by excitations of delocalized states near the Fermi energy dominated by O:3<sub>AB</sub> electron density. The early SCF calculations for  $\text{Cu}_4\text{O}_4$  in a YBCO crystal field indicated that the HOMO<sub>MO74</sub> shows a continuous electron density along the diagonal  $\text{O}_A\text{:O}_B$   $\sigma$ -bonds, while Cu is weakly bonding (fig. 5a)<sup>[8a]</sup> and lead to a  $\text{CuO}_2$  layer extended state chains:

$$\Psi_{\text{HOMO}, \mathbf{k}} = \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} (a(\text{O}_{A_i}:2p_{xy} - \text{O}_{B_i}:2p_{xy}) + b\text{Cu}_i:3d_{xy}) / \sqrt{N} \quad (8)$$

where for  $\mathbf{k}=\mathbf{k}_f=\pm(\pi, \pm\pi, 0)$  show a constant O:2 $p_{xy}$  overlap  $\langle e^{i\mathbf{k}\cdot\mathbf{R}_A}\text{O}_{A_i}:2p_{xy} | e^{-i\mathbf{k}\cdot\mathbf{R}_B}\text{O}_{B_i}:2p_{xy} \rangle$  greater than zero along an in plane diagonal, which focuses 1D transport along that  $(\text{O}_A:\text{O}_B)_{1/2q}$  chain. To change the overlap direction a chain bond must be broken at the cost of an excitation energy,  $h\nu_{\text{ex}} \sim |t|/N$ ,  $N=1/q$ , where  $t \approx 260\text{meV}$  is the single bond exchange integral<sup>[5f]</sup> forming bi-radicals  $(\text{O}_{3A}-\text{O}_{3B})_{N/2} = X^\pm$ . This explains the YBCO<sub>7</sub> orthorhombic to tetragonal phase transition at  $700\text{K}$ <sup>[5g]</sup> when  $q=1/4$ , but at lower T and  $q_{\text{PLD}}=1/24$ ,  $|t|/N = 3017/24 = 125\text{K}$ . At  $298\text{K}$ ,  $X^\pm$  decays at a rate  $1/T_1$  into the two equally populated phases observed, but at  $125\text{K}$  the charge vortices produced by the PLD (fig. 5b) can lead to BKT transitions<sup>[8d,e]</sup> where lattice vibrations focus 1D superconductivity along that in plane diagonal, as found in the bulk<sup>[5b,f,g]</sup>. Overhauser has already suggested that PLD effects may lead to superconductivity<sup>[4g]</sup>.

**Table I:** Crystallographic weights  $\alpha = \cos(\mathbf{Q}\cdot\mathbf{r})$ <sup>[5a,6a]</sup> used in (2) for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $D_{2h}^{17}$ :  $\alpha_M(001) = n_M \cos(2\pi z_M E/E_{\text{Bragg}})$  where  $E_- = E_{\text{Bragg}} = E(M_{\text{edge}})$ ,  $E_+ = E(M_{\text{edge}}) = E_{\text{Bragg}} - DE(\text{eV})$  (fig. 4b, 8), and  $n_M =$  number of equivalent  $M = \text{O}, \text{Cu}, \text{Y}, \text{Ba}$ .

M SITE:	x(a)	y(b)	z(c)
O:1/Cu:1	0/1/2	1/2/1/2	0/0
Ba/O:2	0/1/2	0/1/2	.18/.16
Cu:2	1/2	1/2	.36
O:3A/3B	1/2/0	0/1/2	.38/.38
Y:	0	0	1/2

$\alpha_{\text{O}, \mathbf{k}}(001)$	O:1	2	3A+3B
$E_{\text{Bragg}}=E_+$	1	1.0	-2.8
$1500+E_+$	1	1.9	3.2

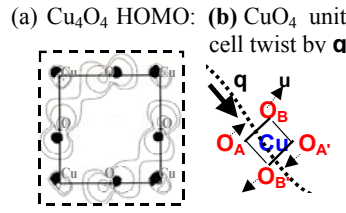
$\alpha_{\text{Cu}, \mathbf{k}, \pm 1}(001)\text{Cu}$ :	1	2
$E_+$	1	-1.3
$150+E_+$	1	-0.7

$f(M=M, \text{O}) = \alpha_M f_M$	HKL
005	005
010	010
322	322
112	112
114	114
114	114
224	224
224	224

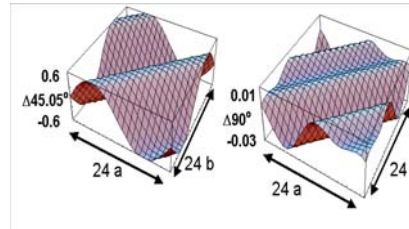
  

$f_M = f_M(E \sin\theta/hc)$	$\alpha_M = n_M \cos((\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_M) = n_M \cos(4\pi E z_{M,C} \sin\theta/hc)$
$1500+E_+$	$\alpha_M = n_M \cos(2\pi z_M E/E_{\text{Bragg}})$



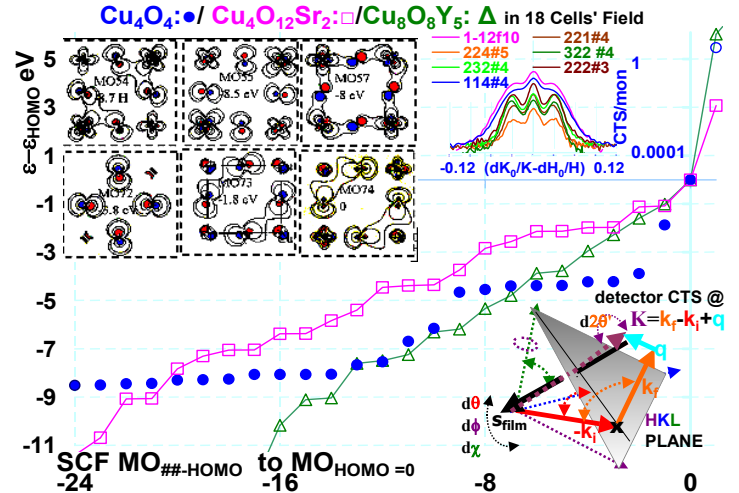
**Figure 5:** Possible PLD source and effects: (a) Electron density in  $\text{Cu}_4\text{O}_4$  HOMO:  $\rho_e \geq 10^{-3}b^{-3}$ <sup>[8a]</sup>. (b) Transverse  $\mathbf{q}_{\text{PLD}}$  (3) that produces twins and  $\text{O}_4$  twists giving rise to charge vortices.

The physical significance of  $\mathbf{q}$  in the film properties may be different from the bulk crystal. However, the observed PLD compare to the additional XRD reciprocal lattice spots assigned to twinning in single crystals<sup>[4k]</sup> and explain the stripes observed in TEM by the periodicity of  $\text{O}_A\text{:O}_A \wedge \text{O}_B\text{:O}_B = 90^\circ \pm 0.02^\circ$  and  $\text{O}_A\text{:O}_A \wedge \text{O}_A\text{O}_B = 45.05^\circ \pm 0.6^\circ$  in the  $\text{CuO}_4$  angles (fig. 5) which remain unchanged only along one ab diagonal (fig. 6) causing an elastic strain  $\epsilon_{(01)} = 1 - \tan(\text{O}_A\text{:O}_A \wedge \text{O}_A\text{O}_B/2) = -0.07\%$  that leads to a preferred twin<sup>[4m]</sup> with possible film buckling and/or stripes<sup>[6d]</sup>.



**Figure 6:** Deviation from  $\text{O}_A\text{:O}_A \wedge \text{O}_A\text{O}_B = \text{atan}(b_0/a_0) = 45.05^\circ$  and  $\text{O}_A\text{:O}_A \wedge \text{O}_B\text{:O}_B = 90^\circ$  due to PLD on  $\text{Cu}_4\text{O}_4$  (fig. 5b).

States near the Fermi energy will interact via the absorption and emission of photons at resonance. Given<sup>[4f]</sup>,  $E = E(\text{Ba}_{L3\text{-edge}}) + E(\text{Ba}_{M3\text{-edge}}) + E(\text{Ba}_{M4\text{-edge}}) + E(\text{Cu}_{L3\text{-edge}}) = 8042\text{eV}$ , (9) states in YBCO have a finite cross section for  $h\nu_{\text{in}} = 8048$  to  $8040\text{eV}$ . Then  $h\nu_{\text{out}} = h\nu_{\text{in}} - E$  can induce  $\Psi_{\text{HOMO}, \mathbf{k}=\pm(\pi, \pm\pi, 0)}$  (fig. 7)<sup>[8a]</sup> absorption which transfers  $\mathbf{k}_f - \mathbf{k}_{\text{free}} \parallel \mathbf{q}$  to the scattering vector  $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$ <sup>[8f,g]</sup>. Thus resonance can and does enhance the sideband amplitude and BKT vortices<sup>[8d,e]</sup>. But, since



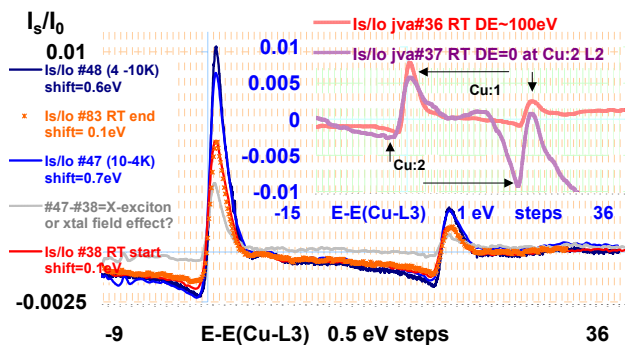
**Figure 7:** Exact SCF MO basis near the Fermi level for different size lamella in 18 unit cells' crystal field with similar energy up to  $\epsilon - \epsilon_{\text{HOMO}} \approx 8\text{eV}$ . Inserts show: the tight binding approximation (8) MO basis with anti-parallel alignment of two diagonal  $3d^9\text{Cu}$ ,  $s=1/2$ ,  $m(d_{x^2-y^2})$  atoms in the HOMO<sub>MO74</sub><sup>[8a]</sup>, how excitations of (8) add  $\mathbf{k}_f - \mathbf{k}_{\text{free}} \parallel \mathbf{q}$  to  $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$ , and XRD plots showing coincident  $sb_{\pm 1}$  that obtain  $q_{xy} = (dK_0/K - dH_0/H)_{sb_{\pm 1}} \approx 2^{-1/2}/24$  in all  $H, K, L \neq 0$   $d(H-K)$  scans.

XRD sidebands due to  $\mathbf{q}$  obtain  $\mathbf{u} \sim 0.04(a, -b, 0)$  independent of  $r(\mathbf{t})$  when  $h\nu_{in} = 7.2, 8.0$  and  $9.5 \text{ keV}$ , the PLD appear to be an intrinsic film property where only the amplitude increases in the presence of resonance excitations.

$I_s/I_0$  peaks enhanced near the  $\text{Cu}_{L_{3,2}}$  edge (fig. 8) as  $E \Rightarrow E_{\text{Bragg}}$  indicate the complexity of the transitions<sup>[7b,c]</sup>:

$\cdot\text{Cu}:2p_{3/2} \leftrightarrow \cdot\text{Cu}:3d_{5/2}$  and  $\cdot\text{Cu}:2p_{1/2} \leftrightarrow \cdot\text{Cu}:3d_{3/2}$ . (10)

Now the advantage of  $I_s/I_0$  over XAS is evident. The Cu:1,2 site contributions are identified by the opposite sign of  $\alpha$  in the  $D^{17}_{D_{2h}}$  group (Table I). Less shielding by  $0.65 \pm 0.05 \text{ eV}$  is detected at Cu:1 than at Cu:2 sites more convincingly than by Cu XAS<sup>[7c, 8b-d]</sup>. Below  $T_c$  a shift of  $0.6 \pm 0.05 \text{ eV}$  and an increase in the Cu:1 peak integrated intensity definitely confirms the formation of X-ray polarons, excitons and/ or new vacancies in Cu:1 3d final states<sup>[7c]</sup>. The  $O_{K\text{-edge}}$  measurements indicate that the O atom shielding changes are of the order of  $\sim 0.2 \text{ eV}$  below  $T_c$  (fig. 4c) and transfer  $\mathbf{k}_{\text{valence}} - \mathbf{k}_{\text{free}}$  from  $\Psi_{\text{HOMO}, \mathbf{k} = \pm(\pi, \pm\pi, 0)}$  by excitation at  $h\nu = k_B T = |t|/N$  near 125K for  $N=24$  and  $|t|=260 \text{ meV}$ <sup>[5f]</sup> as first suggested by the SCF calculations  $\text{HOMO}_{\text{MO74}}$ <sup>[8a]</sup> and first discovered experimentally by XPE<sup>[8h]</sup> in bulk crystals.



**Figure 8:** BC04/04 Cu:L<sub>2,3</sub> edges  $I_s/I_0$  ( $\chi = 5.02$ ,  $\theta = 29.5$ ,  $2\theta' = 65.5^\circ$ ,  $E_{\text{Bragg}} - E(\text{Cu}_{L_{3,2}}) = 150 \text{ eV}$ ) extremes of reversible 12h temperature cycle. Far from the edge, baselines were made to coincide, and the 4-10K energy scale was shifted by  $0.65 \pm 0.05 \text{ eV}$  with respect to the RT for all to coincide at  $E - E(\text{Cu}-L_{3,2}) = 0$ . Inset identifies peaks associated with atoms at Cu:*i* sites by the opposite sign of  $\alpha(\text{Cu}:i, i=1,2)$ <sup>[6a]</sup> (Table I) showing strong enhancement effects as  $E \Rightarrow E_{\text{Bragg}}$ .

#### 4. CONCLUSION

Results obtained using synchrotron radiation measurements indicate that in fabricated  $\text{YBCO}_x$  soft solid nano-films, PLD are present in SC though resolved only in BC films, and XRD resonance effects identify a path for the metal insulator transitions (5) between phases that are also found in bulk YBCO where the intermediate in (5)  $X^\#$  may be associated with  $(O_A \cdot O_B)_{1/2q}$  bi-radical chains formed when changing the direction of diagonal conductivity by resonance X-ray flux effects and/ or by temperature  $T$ .

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