Chemical activity in YBa$_2$Cu$_3$O$_7$ − $\delta$ across the normal to superconducting phase transition

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Chemical activity in YBa$_2$Cu$_3$O$_{7-\delta}$ across the normal to superconducting phase transition

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Abstract

The Gibbs free enthalpy, chemical activity across the transition temperature to superconductivity, T$_c$ in YBa$_2$Cu$_3$O$_{7-\delta}$ is obtained from reciprocally enhanced X-Ray absorbance, XAS and diffraction, XRD data near the Ba L$_{3,2}$ edges’ energy E$_{a}$, and orientations in the X-ray beam for preferred Miller indexed [HKL] planes’ scattering that are enhanced near T$_c$. The standard enthalpy and entropy for the formation of mixed normal metal/superconducting domains above T$_c$, determined individually across the two Ba L$_{3,2}$ edges, to better than a percent accuracy: $\Delta H^e_{\geq} = -220$ meV, and $\Delta S^e_{\geq} = -2$ meV/K when $121 \geq T \geq 92K \approx T_{c1}$, indicate there is energy available to form the mixture and the reduced entropy indicates there is also order increase. Below T$_c$ the standard enthalpy and entropy to form at least two mixed superconducting phases is halved to $\Delta H^e_{\leq} = -86$ meV, $\Delta S^e_{\leq} = -1$ meV/K when $92K \geq T \geq T_{c2}\approx 72K$. Thus reciprocal XAS/XRD enhancement at orientations in the X-ray field, of preferred 2D planes, induced by the transition to superconductivity in the layer solid, indicates one, the importance of the 2D-plane electron density scattering near T$_c$, and two, identifies the 2D-plane chemical activity, by the electron density leading to symmetry allowed excitations, a role similar to that of the electron density in linear bonds for molecular activity.
Introduction

This work uses the Onsager reciprocity relation expected for enhanced X-ray absorption spectroscopy, XAS and co-incident diffraction, XRD at preferred orientations versus temperature, T near the phase transition to superconductivity, T_c including all the layers of YBa_2Cu_3O_{7-δ}, to enrich the literature on layer materials[1,2]. Pauling describes the role played, in the phase transition by resonance between two Cu=O at 90° angles in the CuO_2 layer[1f] which is included in most models that explain the importance of the CuO_2 layer. But, to understand the periodic lattice distortion, PLD effects proposed by Overhausser[2c] and the de Gennes boundary effect arguments[2d] the role played near T_c by other than the CuO and CuO_2 layers is necessary. In YBa_2Cu_3O_{7-δ} and Bi_2Sr_2Ca_2O_{3+δ}, the appearance of superconductive domains has been deduced by the presence of Abrikosov vortices at ~60 K above T_c[2h,p], when it is determined by bulk measurements of heat capacity and susceptibility[1g,2k-o]. At temperatures where the thermal fluctuation energy is comparable with the elastic and the pinning energy of vortices other stabilizing interaction must be present. This work obtains the chemical activity, measured by the standard Gibbs free enthalpy for the formation[2w] of normal/superconducting mixed states using reciprocally enhanced XAS and preferred XRD reflections data[1a-i] versus temperature to identify how the different layers in YBa_2Cu_3O_{7-δ} are involved across T_c.

Experimental

The published enhanced absorbance and diffraction data used was obtained by XAS and XRD synchrotron measurements at DOE National Laboratories SLAC-SSRL, LBL-ALS[1a-e]. I(hν)=(detector counts)/(monitor counts) versus near energy, E_a (fig. 1-4) for different YBa_2Cu_3O_{7-δ} samples are used: a single crystal grown by CT Lin[1k] and NdBa_{1.9}Nd_{0.1}Cu_3O_{7-δ} powder grown by KK Singh at IRC for Superconductivity, Cavendish Laboratory[1b], and 30nm YBa_2Cu_3O_{7-δ} films on [001] SrTiO_3, grown by MA Navacerrada at the Complutense University[1e]. Calibration with CuO standards allow E_a comparison versus T to better than ±¼eV. Incident and transmitted X-Rays near a constituent resonance energy, E_a along k_0, are scattered along k_s with the polarized electric field ε_0, ε_s in the plane of incidence, and scattering Q=|k_s-k_0|=4π n(E_a) E_a sinθ_{Bragg}/hc=G_{[HKL]}=2π((H/a)^2+(K/b)^2+(L/c)^2)^{1/2}, leads to Stenström shifts due to index of refraction n(E_a), ∆E_a=E_a(n(E_a)-1)/sin^2θ[1i], and its critical oscillations[2q] near phase transitions (fig. 4b). Orientation in the X-ray beam cryostat is given by β_{[001]}=k_0^caxis, and
the field projection \( \phi_{[001]} = \varepsilon_{[001]} \cdot a_{\text{axis}} \), and \([\text{HKL}]\) reflections occur when the Bragg condition,

\[
\sin\theta_{\text{Bragg}} = 2\pi L/c/Q \cos\beta_{[001]} \left(1 - (2\pi L/c/Q)^2\right)^{1/2} \sin\beta_{[001]} \cos(\phi_{[001]} - \phi_{[\text{HKL}]})
\]

is satisfied (Table I).

**Discussion**

The strong Ba L\(_{3,2}\)-\(E_a\) enhanced absorbance data across \(T_c\) (fig. 2) is used to identify the chemical activity near the BaO layer, which is consistent with the other elements’ edge enhancement\([1a-d]\) (fig. 1, 3, 4). The growth and chemical activity in a solid is determined by the 2D reactive \(Q=[\text{HKL}]\) reflection planes’ electron density, in the highest occupied and lowest unoccupied extended states \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\), which also determine the transition temperature to superconductivity, in a manner similar to the role of reactive linear bonds in molecular activity. Accurate data for transitions from the constituent elements core states to the lowest unoccupied extended states, \(E_{\text{LUMO}}\) near the Fermi energy, in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\), measured versus \(T\) in cycles from room temperature (RT) to liquid He (4K) and back\([1b-e]\) (fig. 1-4):

\[
\delta\varepsilon\varepsilon(\text{core atomic state}) \Rightarrow |f(E_{\text{LUMO}})>,
\]

describe the transition probability by the induced moment squared:

\[
|M_{Q,a}|^2 = |\langle i|\exp(-i\mathbf{k}_0 \cdot \mathbf{R}_a)\varepsilon_0 \delta\mathbf{R}_a|f\rangle < f|\exp(i\mathbf{k}_s \cdot \mathbf{R}_a)\varepsilon_s \delta\mathbf{R}_a|i\rangle|,
\]

when \(\varepsilon_0, \varepsilon_s\) have non-zero components in the reflection plane \(Q\) at the Bragg condition. \(\delta\mathbf{R}_a\) is the charge displacement at atom \(a\) by the polarized synchrotron radiation, and the final states obey the symmetry selection rules. The extended states, may be described in a first order approximation by the superposition of individual layer wave functions, \(\Psi_{\text{layer}}\) obtained by self consistent field molecular orbital calculations, weighted by a factor, \(\alpha_{Q,\text{layer}}\) in a tight binding approximation\([1f,h]\).
\[ |Q\rangle = \sum \{ a_{Q,CuO_2} \Psi_{CuO_2} + a_{Q,BiO} \Psi_{BiO} + a_{Q, SrO} \Psi_{SrO} + a_{Q, Ca_l} \Psi_{Ca_l} \} \sqrt{N}. \] (1.2)

At energies far from resonance absorption, and at temperatures far from a phase transition, XRD is analyzed using the kinematical approximation for \( I(Q) = I_0 / I_0 \) to obtain the scattering power \( I_{Q} \):

\[ S_Q = \int_{Q \pm 2(WHH)} I(Q') dQ' / \int_{Q \pm 2(WHH)} dQ' = |F_Q|^2 A_m(E, Q) \] (2)

where the total material absorption, \( A_m \), depends on the radiation path, \( d / \sin \theta \) and its tabulated linear absorption coefficient \( d = 6.4 \pm 1 \mu m \), for CT single crystal thickness where uncertainty, especially at the Y K-edge is introduced by strong XRD enhancement and index of refraction oscillations (fig. 4b). In three dimensional solids, both the scattering power and chemical activity at a site \( R \) depend on the lattice potential:

\[ V(R) = \sum_{[HKL]} V_{[HKL]} e^{i Q \cdot R}, \] (2.1)

where the Fourier component, \( V_{[HKL]} \) is proportional to \( f_{Q,l} \):

\[ F_Q = \sum_{l} f_{Q,l} \alpha_{Q,l} \] (2.2)

Contributions from constituent element electron density scattering power, \( f_{Q,l} \) (\( f_{0,Q,l} \) are tabulated at energies far from a resonance absorption \( [2g] \)) and \( \alpha_{Q,l} = \exp(i R_l q + \phi_l) \). In layer materials the occupied sites \( R_l \) are usually displaced from the ideal Space Group site \( R_l^0 \), by \( \delta_l = \sum q u_q \exp(i (R_l q + \phi_q) \), due to periodic lattice distortions, PLD chemical waves, \( q = (q_x, q_y, q_z) \), then:

\[ \alpha_{Q+q,l} = \sum_{\text{unit cell equivalent}} l \exp(i (R_l + \delta_l) \cdot Q), \] simplified by the Jacobi-Anger theorem \( [2c,e] \):

\[ \alpha_{Q+q,l} = \sum_{l, q,n=0,\pm1} J_n(z_{q,Q} \cdot R_l + \phi_q), \]

identifies the Bragg reflections at \( \sum_{l, q}(Q+nq) \cdot R_l + \phi_q = 2\pi m \), (m, n = integers), when \( n \) PLD sidebands about a center band, are separated by \( q \cdot Q / |Q| \), the \( J_n(z_{q,Q}) \) are 1\(^{st}\) order Bessel functions with \( Q \) dependent argument \( z_{q,Q} = u_q \cdot Q \), evaluated from the relative sideband to center band intensity, \( I_0 / I_0 = |J_n(z_{q,Q}) / J_0(z_{q,Q})|^2 \) and there may be more than one \( |q| << |Q| \). The PLD waves in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\), \( q_{xy} = 2\pi / 12(a^2 + b^2)^{1/2} \) determine the reflection plane Q scattering power \( [1e] \) and the chemical activity by interference between transmitted, \( T_j \) and reflected the \( S_j \) waves, at the \( j^{th} \)
layer (fig. 1). Near an absorption energy, $E_a$ resonant scattering terms and neighbor, $l$ dependent extended X-Ray absorption fine structure, XAFS $\chi$ in condensed matter respectively obtain\cite{2a,b}:

$$F_{Q,a} = A_{0,Q} + \sum_l C_{l,Q} \tag{2.3}$$

where,

$$A_{0,Q} = F_0^0 + \alpha_{Q,a} (f^0 + i f^0)_{Q,a}, \quad F_0^0 = \sum_l \alpha_{Q,l} f_0^l, \quad C_{l,Q} = f^l_a \alpha_{Q,a} (\chi_+' + i \chi_-') \tag{2.3}$$

\((f^0 + i f^0)_{Q,a} = |\mathbf{M}_{Q,a}|^2 r_0 (\Delta_a + \chi_+' a) / \Gamma_a / [\Delta_a^2 + \chi_+'^2] \), and \(1-n(E_a) = (f^0 - i f^0)_{Q,a} \rho_Q r_0 h^2 c^2 / 2\pi E_a^2 \),

and the enhancement is given by:

$$|F_{Q,a}|^2 - |F_0^0|^2 = F_0^0 \sum_l \alpha_{Q,l} (2\Delta_a + \chi_+' a) / \Gamma_a |\mathbf{M}_{Q,a}|^2 / [\Delta_a^2 + \chi_+'^2 + \chi_-'^2] \tag{2.4}$$

Thus enhancement and index of refraction oscillations depend on $|\mathbf{M}_{Q,a}|^2$, the classic single electron scattering Thompson radius $r_0 = e^2 / mc^2 = 2.82E-5\text{Å}$, the resonance absorption line width, $\Gamma_a = \text{WWH}$ at half amplitude, the separation from resonance $\Delta_a = (\Delta E_L + E_a - h\nu) / \Gamma_a$, where $\Delta E_L$ is the Lamb shift, and the electron density $\rho_Q \approx |\sum_l \alpha_{Q,l} f_0^l| / v_c$ where $v_c$ is the volume of the unit cell\cite{2a}, and indicate that transitions (1) vary across $T_c$ due to enhanced electron density-structure interactions in all the layers of YBa$_2$Cu$_3$O$_{7-\delta}$ (fig. 1-4).

The enhanced XRD [001] reflection (WHH $\leq 1\text{eV}$) versus Cu L$_{3,2}$-$E_a$ (fig. 1a) is used to identify the respective layer contributions by the sign and magnitude of $\alpha_{\text{CuO}}$ and $\alpha_{\text{CuO}_2}$ (Table I) which is in agreement with Cu K-edge XRD-DAFS assignments\cite{2b}, but enhanced XAS near the Cu K-$E_a$\cite{1b} is not resolved at co-incident reflections orientations (fig. 4a, Table I) probably because the contribution from $\alpha_{\text{CuO}}$ and $\alpha_{\text{CuO}_2}$ cancel and/or $|\mathbf{M}_{Q,a}|^2$ is not symmetry allowed. Enhanced XAS near the Y K-$E_a$ by co-incident XRD [00L] and [22L] reflections (fig. 4b, Table I) indicate that $|\mathbf{M}_{Q,a}|^2$ is allowed by symmetry, and there is strong negative enhancement (2.4) at the orientation $\beta=0^\circ$ for Y K-edge. The accurate data near the Ba L$_{3,2}$-$E_a$, at orientation $\beta=0^\circ$ obtain $\mu_{0m} = \mu_0 A_m = 2.2$ and 1.4 independent of T, which includes the total material loss, $A_m$, in agreement with $d=6.4\mu m$, and the XAFS, $X_{k,T}$ function\cite{2u} (fig. 2):

$$\ln(A_{E>E_a})_{k,T} = \ln(\mu_{0m,T}(1+X_{k,T})) = \ln(\mu_{0m,T})(1 + (X_{k,T} - \chi_{k,T}^2 + \chi_{k,T}^3)/\ln(\mu_{0m,T})) \tag{2.5}$$

At $\beta=10^\circ$, the enhancement $e_{T,k} = \ln(A_{T,k}/A_{121,K,k})$ is maximum with a deviation versus k (fig. 2c):

$$\Delta e_{k,T} = e_{T,K} / e_{T_1,K} = 1 + (X_{k,T} - \chi_{k,T}^2 + \chi_{k,T}^3)/\ln(\mu_{0m,T}/\mu_{0m,T_1}) \tag{2.6}$$
that is independent of \(k=(2m_e(E-E_{\text{edge}})/\hbar^2)^{1/2}>4/\text{Å}\), i.e., the XAFS oscillating terms’ contributions cancel out, indicating, within the accuracy of the measurements that there is no structure change across \(T_{c1}\) at all orientations, as already determined by Nguyen\(^{[1b,d]}\), and the increased absorbance temperature dependence by scattering is the Onsager reciprocal relation to the increased scattering by absorbance, which is determined by the transition moment \(|\mathbf{M}_{0d}|^2\), when \(\epsilon_0, \epsilon_a\) have non zero components in the \(Q=[117]\) and \([118]\) planes (Table I).

The temperature dependence of \(\mu_{0m,T}(\beta=10^6)\) in the interval \(121K > T > 93K\), indicates a mixture of phases is present, say:

\[
\text{N(normal metal)}_{T>121K} \Leftrightarrow \text{M(mixed)}_{121K \geq T \geq 93K} \Leftrightarrow \text{SC}_1(\text{superconducting})_{T \leq 93K},
\]

where the mixed state absorbance (fig. 2e), and activity are the sum of contributions\(^{[2w]}\),

\[
<\mathbf{A}_{E>\text{Edge},T}>=\mu_{0m,T}(M)=x_{SC1}\mu_{0m(SC1)}+x_N\mu_{0m(N)}, \quad \text{and} \quad a_M=x_{SC1}a_{SC1}+x_Na_N,
\]
a = 1 for pure solids, and \(x_{SC1}\) is the mole fraction of the superconducting state in (3). Then:

\[
\exp(-\Delta G_{\neq}^F/k_BT)=(x_{SC1}/x_N)_{121K \geq T > T_{c1}}=[<\mathbf{A}_{E>\text{Edge},T}> - <\mathbf{A}_{E>\text{Edge},121K}>]/[<\mathbf{A}_{E>\text{Edge},T_{c1}}> - <\mathbf{A}_{E>\text{Edge},T}>]
\]

obtains the standard state free enthalpy of formation, \(\Delta G_{\neq}^F\) at the two edges to better than 1% reproducibility (fig. 2f), indicating the involvement of the BaO layer chemical activity, by \(\Delta H_{\neq}^F=-220\text{ meV}\) and \(\Delta S_{\neq}^F=-2\text{ meV/K}\) and that energy and symmetry are gained in (3). This compares with energy necessary for the reported motion in \(\text{YBa}_2\text{Cu}_3\text{O}_7-x\), across \(T_c\) by anelastic relaxation time measurements, \(t=t_0\exp(-W_i/k_BT)\) where \((t_0, W_i)=(4E14, 160\text{meV})\) and \((2E-13, 140\text{meV})\)\(^{[2r]}\) which use a fraction of the energy gained for the activation dynamics of atomic oxygen jumps between a, b lattice sites in the \(\text{CuO}_2\) layer, at the phase transition that appears to be similar to the correlated and uncorrelated oxygen octahedral rotations in the parent compound, \(\text{SrTiO}_3\) at the 103 K phase transition\(^{[2a]}\), leaving an energy balance, \(W_i+\Delta H_{\neq}^F+103k_B\approx-50\text{ meV}\) to form a stable mixed state. Pauling describes the contribution to superconductivity in layer cuprates, by resonance between 2 pure \(\text{Cu}=\text{O}\) covalent bonds forming 90° to each other, or 4 half covalent and half ionic\(^{[10]}\), which is equivalent to an electron density distribution in the \(\text{Cu}_4\text{O}_4\) highest occupied states (HOMO) obtained by self consistent field, SCF calculation for the \(\text{CuO}_2\) layer in a perfect cuprate lattice using MOTECC-91 codes (fig. 1b)\(^{[1f]}\), and similar SCF calculations using METTEC codes for a cluster of 19 unit cells by Sahibudeen\(^{[1e]}\) show that the observed PLD with \(q_{xy}=2\pi/12(a^2+b^2)^{1/2}\) in the 30 nm film can transfer charge between the \(\text{CuO}_2\) and neighboring layers. Additional ordering present below \(T_{c1}\) is evident in many measurements.
e.g., $[2t, 1b]$ and a mixture of superconducting phases, say SC$_1$ and SC$_2$ is indicated by the rise in A above $T_{c1}$ (fig. 2e) where the mixture:

$$SC_1(\text{superconducting})_{T_{c1} \geq T < T_{c2}} \leftrightarrow SC_2(\text{superconducting})_{T < T_{c2} = 71.2K},$$

is described by the Gibbs free enthalpy of formation:

$$-\Delta G^{\neq} / k_B T = \ln(x_{SC2}/(1-x_{SC2}))_{T_{c1} \geq T < T_{c2}} \equiv \left[ A_{E^{\neq} \text{Edge},T} - A_{E^{\neq} \text{Edge},T_{c1}} \right]/ \left[ A_{E^{\neq} \text{Edge},T_{c2}} - A_{E^{\neq} \text{Edge},T} \right],$$

and indicates that the chemical activity is halved below $T_{c1}$, $\Delta H^{\neq} = -86$ meV, $\Delta S^{\neq} = -1$ meV/K (fig. 2f), and that the mixture favors ordering.

Thus enhanced XAS/XRD measurements indicate that the Cu:(nd$_{5/2,3/2}$), Ba:(nd$_{5/2,3/2}$), O:(np$_{1/2,3/2}$) and Y:(np$_{1/2,3/2}$) electron density contribute significantly to E$_{\text{HOMO}}$ and E$_{\text{LUMO}}$ interactions near $T_c$, and that there is need for vacuum sites in YBa$_2$Cu$_3$O$_{7-\delta}$ (insert fig. 1a) for e$_2$, periodic phonon interactions that lead to BCS type superconductivity$^{[2v]}$. But, the motion is more complex in YBa$_2$Cu$_3$O$_{7-x}$, than in the parent SrTiO$_3$ perovskite due to barriers introduced by an incomplete oxygen octahedral crystal field. The role of $|\mathbf{M}_Q|^{2}$ near $T_c$ suggests the possibility to induce the phase transition by photochemical excitation at preferred orientations as has been done in organic superconductors$^{[1m]}$ by cooling the material subject to radiation at preferred orientations to induce transitions between the states:

$$|E_{\text{HOMO}} > \leftrightarrow |E_{\text{LUMO}} >,$$  \hspace{1cm} (4)

separated in energy by the shifts observed at say the Cu L$_{3,2}$ $E_a$, of 0.4 eV (fig. 1a) across $T_c$.

**Conclusion**

Chemical activity in YBa$_2$Cu$_3$O$_{7-\delta}$, induced near the transition temperature to superconductivity leads to reciprocally enhanced XAS and XRD, at preferred orientations, and identifies the importance of scattering between all the layers at the phase transition, independent of the any prevalent model.

**Acknowledgements**

The support for work$^{[1]}$ at DOE National Laboratories LBL-ALS, and SLAC-SSRL, IBM Kingston (1991), Trinity and Lucy Cavendish Colleges, Cambridge, and IRC for Superconductivity, Cavendish Laboratory, NSF, and the H. and C. Dreyfus grants at SJSU with valued colleagues (E Clementi, O Stradella, G Corongiu, L Nguyen, CM Burch, ML Chen, MA
Navacerrada, H Sahibudeen, KK Singh, C Chigvinadze, CT Lin and WY Liang) is gratefully acknowledged.
Table I: YBa$_2$Cu$_3$O$_{7-\delta}$ scattering parameters near $E_a$. The laboratory parameters which lead to reciprocally enhanced absorption and scattering are given for orientations in the X-Rays’ field, $\beta_{[001]}=k_0^c\hat{c}$, and $\phi_{[001]}=\epsilon_{[001]}^a\hat{a}$ when $(\pi/2-k_0^G)^{[HKL]}-\theta_{\text{Bragg}}$ is within the XRD line width$^{a-d}$.

The crystal parameters ($a=3.82$, $b=3.89$, $c=11.68$ Å in $D_{2h}^1$ Space Group) and $f^0_1$ Cromer Mann Atomic Scattering Tables$^{[2g]}$, obtain $\theta(E_a)$ and $F_0^Q$ when the Bragg condition is satisfied for an XRD $[HKL]$ reflection plane.

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<td>measured $E_a$ (eV)</td>
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<td>$\hat{\theta}_{\text{bragg},E_a}$ (°)</td>
<td>83.39</td>
<td>29.50</td>
<td>55.62</td>
<td>58.89</td>
<td>80</td>
<td>71</td>
<td>37</td>
<td>65</td>
<td>85</td>
<td>60</td>
<td>62</td>
<td>45</td>
</tr>
<tr>
<td>$\epsilon_{[001]}^G[110]$ (°)</td>
<td>0.4</td>
<td>24.6</td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
<td>9.0</td>
<td>19.5</td>
<td>11.5</td>
<td>7.7</td>
<td>13.2</td>
<td>19.5</td>
<td>7.5</td>
</tr>
<tr>
<td>$% \Delta \theta_{\text{bragg}}/\theta$</td>
<td>5%</td>
<td>-17%</td>
<td>-1%</td>
<td>0%</td>
<td>-11%</td>
<td>-4%</td>
<td>2%</td>
<td>1%</td>
<td>0%</td>
<td>-1%</td>
<td>1%</td>
<td>-2%</td>
</tr>
<tr>
<td>$% \Delta E_{\text{bragg}}/E$</td>
<td>-1.1%</td>
<td>15.4%</td>
<td>0.5%</td>
<td>0.0%</td>
<td>1.5%</td>
<td>1.6%</td>
<td>-1.7%</td>
<td>-0.4%</td>
<td>0.0%</td>
<td>0.7%</td>
<td>-0.5%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

a. Enhanced XRD $I_{[001]}$ reflection, near O K, and Cu L$_{2,3}$-$E_a$, proportional to $\alpha_{a,Q} F^0_Q F^2_0 \alpha_1^2$ is observed when deviations $\Delta \theta/\theta$, and $\Delta E/E$ are within the scattering line widths in (2.3) of the order of 10% to 20% (fig. 1a, 3a), and fluorescence is negligible at 20.

b. Near the Ba L$_{3,2}$-$E_a$ the scattering enhancement of absorbance appears as an increase in A, and $n(E_a)$ critical oscillations$^{[1b]}$.

c. At the Cu K-edge ($\alpha_{\text{Cu}(1)} + 2\alpha_{\text{Cu}(2)})F^0_Q$ mostly cancel.

d. Near the Y K-$E_a$ the [00 33] and [00 23] at the respective orientations $\beta_{[001]}=0$, 45° introduce shifts and $n(E_a)$ critical oscillations.
List of Figures

Figure 1: YBa$_2$Cu$_3$O$_{7-δ}$ 30 nm film on SrTiO$_3$ $^{[1]}$: (a) Temperature cycle of XRD $I_{[001]}$ reflection enhanced near the Cu L$_{3,2}$-E$_a$ ($ΔQ_{[001]}$ ≈ 0.01 to 0.03 Å$^{-1}$)$^{[1e]}$, over 24 h in the JB Kortright chamber at DOE-LBL-ALS$^{[2]}$, indicates edge shifts of ~0.4 eV and intensity doubling below $T_c$ where a c-axis decrease below $T_c$ of 0.1$^{[2]}$ would propagate to a further decrease in $Δ\theta/θ_{Bragg}$ (Table I) and therefore $I_{[001]}$. Cartoon insert describes the layer stacking in the ideal $D_{4h}$ space group$^{[2i,j]}$ with unit cell sites indicated by: open square □: front, closed square ●: back, and presumed element occupation by different shades; ▬: Ba, ▬: Cu, ▬: Y, ▬: O, and ___: vacuum sites which are important for synchronized and unsynchronized motion between occupied sites, and the layers orientation relative to the incident X-Rays’ $β_{[001]} = c^*I_0$. (b) Cu$_4$O$_4$ electron density for the molecular basis set for E_HOMO and E_LUMO obtained by self consistent crystal field calculations of layer cuprates using MOTECC-91 codes$^{[1f]}$, describe the $σ$-bonded O:O chains responsible for transport in different representations which also include $p_z$ molecular orbital symmetry within 10 eV of Rydberg states.

Figure 2: Single crystal CT-YBa$_2$Cu$_3$O$_{7-δ}$ Ba L$_{3,2}$-edge absorption, A enhanced by reciprocal scattering near $T_c$ at certain orientations$^{[1b]}$: (a) Near edge absorbance, $A(T, β_{[001]})$ versus $E_a$, at different $T$ near $T_c$ with $β_{[001]}$=10±1$^o$; —: 121 to 100K, —: 99 to 95 K, —: 93 to 92K, —: 88 to 70K, and —: 69 to 56K, and when $β_{[001]}$=0, and 5±1$^o$ —, and — respectively between $T=121$ to 56K $A$ appear unchanged. (b) $\ln(\Delta_δ/\Delta_{E_a})=\ln(μ_0(1+X)/μ_0(1))$ versus $E>E_a$. (c) Enhancement deviation $\Delta e_{k,T}$ = $\ln(A_{97K}/A_{93K})/\ln(A_{93K}/A_{121K})$-1 versus $|k|=√(2m_e(E-E_{edge})/\hbar^2)$. (d) Cartoons of layer orientation relative to incident, transmitted and scattered X-Rays, $I_{0T}, I_{0T+1}, S_j$, respectively. (e) Absorbance averaged over all $k$ (230 data points at each $T$), $<A>$, versus 1/$T$ near $T_c$ when $β_{[001]}=10±1^o$. (f) Ratio, $\ln(x_{SC}/(1-x_{SC}))$ versus 1/$T$ used to obtain the standard free enthalpy for the formation of mixed states, by linear fits. For $T$$≥$T$_c1=92K$: E$>$E$_{L3}$+, E$>$E$_{L2}$+, and for T$_{c1}$≥T$≤$T$_{c2}$$≈$71K: E$>$E$_{L3}$+: E$>$E$_{L2}$: E$>$E$_{L2}$:. For $T$$≥$ 92K the fit accuracy, $R^2=0.99$ is better than for 92$>$T$>71K, of $R^2=0.93$.

Figure 3: YBa$_2$Cu$_3$O$_{7-δ}$ 30 nm film on SrTiO$_3$ $I_{[001]}$ for reversible temperature cycle near O K-$E_a$, $ΔQ_{[001]}$ ≈ -0.04 to 0.06 Å$^{-1}$$^{[1i]}$. Sites’ are identified by the phase $α_Q$, sign for the enhancement (Table I) in agreement with the literature$^{[2m]}$. Changes in $I_{[001]}$ below $T_c$ suggest state occupation changes below $T_c$.

Figure 4: Single crystal CT-YBa$_2$Cu$_3$O$_{7-δ}$ $A$$^{[1b]}$: (a) Cu K-$E_a$ and. (b) Y K- K-$E_a$. Critical index of refraction $n(E_a)$, oscillations, and negative/positive enhancement indicates the element involvement near $T_c$ (Table I).
References


Figure 1(a)

YBa$_2$Cu$_3$O$_{7-\delta}$ 30nm film on [001]SrTiO$_3$

I$_{[001]}$ near Cu- $L_{3,2}$, $E_a$ Temperature Cycle

- Initial RT – 4K – Final RT

$\Delta Q(1/Å) = 2\pi [2 \sin(2\theta(65.5°) - \theta(29.5°))/\lambda - 1/\epsilon ]$

$F_0^{[001]} \propto F_0^{[001]} \alpha_{CuO}$

$F_0^{[001]} \alpha_{CuO^2}$

0.8

$\sum_j T_j + 1 = A$

Figure 1(b)

MO$_{74}$
$m=53,54$

63,64

66,67

HOMO

(H)

$\epsilon_{m}$

-0.1

-0.4

-0.7

-1

$m=53,54,55,56,57,58,59,63,64,66,67,71,73,74$
$\beta \approx 10^\circ$, $T(K) = 121 - 100, 99 - 95, 93 - 70, 70 - 56$

$\beta = 5^\circ$, $T(K) = 121 - 56; \beta = 0^\circ$, $T(K) = 121 - 56$

$\Delta G^{\neq} > /k_{B}T = 2531/T - 25$

$\Delta G^{\neq} < /k_{B}T = 773/T - 9.7$

$\Delta G^{\neq} >> /k_{B}T = 1247/T - 15$

$\Delta G^{\neq} < /k_{B}T = 5257 - 26$

$\Delta G^{\neq} >> /k_{B}T = 5251 - 26$

$\Delta G^{\neq} < /k_{B}T = 5255 - 25$

$\ln(x_{SC}/(1-x_{SC}))$
Figure 3

$YBa_2Cu_3O_{7-\delta}$ 30nm film on [001]$SrTiO_3$

Temperature Cycle:
- $\$: Initial RT;
- $\$: to 4K;
- $\$: to 44K;
- $\$: to RT

$\Delta Q = 2\pi (2\sin(2\theta(162.4^\circ) - \theta(83.39^\circ))/\lambda - 1/c)$
Figure 4:

(a) \( A(\text{Cu K, 100K}) \)

\( \beta = 0^\circ, 10^\circ, 15^\circ, 25^\circ, 30^\circ, 45^\circ \)

\( \mu_{0m} = 1.15 \)

8.970 9.015 (keV) 9.015 9.215

(b) \( A(\text{Y K, 65K, } \beta) \cdot dA(\text{Y K, } \beta = \pi/4, T) / dE \)

\( \beta = 0^\circ, 5^\circ, 20^\circ, 45^\circ \)

\( n(E_a) \) oscillation

98K 95 92 89 86.6 84.7 69.5 57.5 47 38.9

A/eV 0.03 0.02

8.970 9.015 (keV) 17015 17065 eV 17015 17065 eV