Chemical activity in YBa2Cu3O7 − δ across the normal to superconducting phase transition

Juana Vivó Acrivos
San Jose State University, juana.acrivos@sjsu.edu

Follow this and additional works at: https://scholarworks.sjsu.edu/chem_pub

Part of the Physical Chemistry Commons

Recommended Citation

This Article is brought to you for free and open access by the Chemistry at SJSU ScholarWorks. It has been accepted for inclusion in Faculty Publications, Chemistry by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.
Chemical activity in YBa$_2$Cu$_3$O$_{7-\delta}$ across the normal to superconducting phase transition

JV Acrivos,

San José State University, San José CA 95192-0101

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 $E_{\alpha}$, 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: $\Delta H^\ne_{\ge} = -220$ meV, and $\Delta S^\ne_{\ge} = -2$ meV/K when $121 \ge T \ge 92$K $\approx T_{c1}$, 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 $\Delta H^\ne_{\le} = -86$ meV, $\Delta S^\ne_{\le} = -1$ meV/K when $92$K $\ge T \ge T_{c2} \approx 72$K. 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 Overhauser[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_2Cu_3O_{10+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)⁰, leads to Stenström shifts due to index of refraction n(E_a), ΔE_a=E_a(n(E_a)-1)/sin²θ[1i], and its critical oscillations[2a] near phase transitions (fig. 4b). Orientation in the X-ray beam cryostat is given by β_{[001]}=k_0^\wedge c_{axis}, and
the field projection $\phi_{[001]}=\varepsilon_{[001]}^a a_{axis}$, and [HKL] reflections occur when the Bragg condition, 
\[
\sin\theta_{\text{Bragg}}=2\pi L/c/Q \cos\beta_{[001]}-(1-(2\pi L/c/Q)^2)^{1/2} \sin\beta_{[001]} \cos(\phi_{[001]}-\phi_{[\text{HKL}]}),
\]

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):

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

e.g.,

\[
|i,\text{O}(1s)^2> \Leftrightarrow |f(E_{\text{LUMO}},\text{O}(1s)^2\text{np})>,
\]

\[
|i,\text{Y}(1s)^2> \Leftrightarrow |f(E_{\text{LUMO}}, \text{O}(1s)^2\text{np})>,
\]

\[
|i,\text{Cu..}(2p_{3/2})^4(2p_{1/2})^2(3d)^{10}\text{to}(3d)^9\text{nd}_{5/2})> \Leftrightarrow |f(E_{\text{LUMO}}, \text{Cu..}(2p_{3/2})^4(2p_{1/2})^2(3d)^{10}\text{to}(3d)^9\text{nd}_{5/2})>,
\]

\[
|i,\text{Cu..}(2p_{3/2})^4(2p_{1/2})^2(3d)^{10}\text{to}(3d)^9\text{nd}_{3/2})> \Leftrightarrow |f(E_{\text{LUMO}}, \text{Cu..}(2p_{3/2})^4(2p_{1/2})^2(3d)^{10}\text{to}(3d)^9\text{nd}_{3/2})>,
\]

\[
|i,\text{Ba..}(2p_{3/2})^4(2p_{1/2})^2> \Leftrightarrow |f(E_{\text{LUMO}}, \text{Ba..}(2p_{3/2})^4(2p_{1/2})^2\text{.}(\text{nd}_{5/2})>,
\]

\[
|i,\text{Ba..}(2p_{3/2})^4(2p_{1/2})^2> \Leftrightarrow |f(E_{\text{LUMO}}, \text{Ba..}(2p_{3/2})^4(2p_{1/2})^2\text{.}(\text{nd}_{3/2})>,
\]

describe the transition probability by the induced moment squared:

\[
|M_{Qa}|^2 = |<i|\exp(-i\mathbf{k}_0\cdot\mathbf{R}_a)\varepsilon_0\delta\mathbf{R}_a|f><f|\exp(i\mathbf{k}_0\cdot\mathbf{R}_a)\varepsilon_0\delta\mathbf{R}_a|i>|,
\]

when $\varepsilon_0$, $\varepsilon_a$ 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$^{[1f,h]}$.  

3
\[ |Q| = \sum \{ \alpha_{Q,CuO} \Psi_{CuO} + \alpha_{Q,BiO} \Psi_{BiO} + \alpha_{Q,SrO} \Psi_{SrO} + \alpha_{Q,Ca} \Psi_{Ca} \}/\sqrt{N}. \] (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\[2a]\:

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

where the total material absorption, \( A_m \) depends on the radiation path, \( d/\sin \theta \) and its tabulated linear absorption coefficient\[2g]\; 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:

\[
V(R) = \Sigma_{[HKL]} V_{Q=[HKL]} e^{iQ\cdot R}, \quad (2.1)
\]

where the Fourier component, \( V_{[HKL]} \) is proportional to\[2a]\:

\[
F_Q = \Sigma_{\text{lattice sites}} f_{Q, l} \alpha_{Q, l} \quad (2.2)
\]

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 \( \alpha_{Q, l} = \exp(iR_{r, l} \cdot Q + \phi) \)). In layer materials the occupied sites \( R_{l} \) are usually displaced from the ideal Space Group site \( R_{l}^0 \), by \( \delta_l = \Sigma_q u_q \exp(i(R_{r, q} + \phi)) \), due to periodic lattice distortions, PLD chemical waves, \( q=(q_x, q_y, q_z) \), then:

\[
\alpha_{Q+q, l} = \Sigma_{\text{unit cell equivalent}} l \exp(i(R_{r, l} + \delta_l) \cdot Q),
\]

simplified by the Jacobi-Anger theorem\[2c,e]\:

\[
\alpha_{Q+q, l} = \Sigma_l \Sigma_{q, n=0, \pm 1} J_n(z_{q, Q}) \exp(i(Q+nq) \cdot R_{r, l} + \phi_q) \exp(iR_{r, q} \cdot Q) = 2\pi n, \quad (m, n = \text{integers}), \quad \text{when} \quad n \text{ PLD sidebands about a center band, are separated by} \quad q \cdot Q/|Q|, \quad \text{the} \quad J_n(z_{q, Q}) \quad \text{are 1st order Bessel functions with} \quad Q \quad \text{dependent argument} \quad z_{q, Q} = u_q \cdot Q, \quad \text{evaluated from the relative sideband to center band intensity,} \quad I_n/I_0 = |J_n(z_{q, Q})/J_0(z_{q, Q})|^2 \quad \text{and there may be more than one} \quad |q|<<|Q|. \quad \text{The PLD waves in} \quad \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}, \quad q_{xy}=2\pi/12(a^2+b^2)^{1/6} \quad \text{determine the reflection plane} \quad Q \quad \text{scattering power}[1e] \quad \text{and the chemical activity by interference between transmitted,} \quad T_j \quad \text{and reflected the} \quad S_j \quad \text{waves, at the} \quad j^{\text{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 \[^{[2a,b]}\]:

$$F_{Q,a} = A_{0,Q} + \sum_{l} C_{l,Q}, \quad \text{(2.3)}$$

where,

$$A_{0,Q} = F_{Q}^{0} + \alpha_{Q,a} (f^* + i f^*)_{Q,a}, \quad F_{Q}^{0} = \sum_{l} \alpha_{Q,l} F_{Q,l}, \quad C_{l,Q} = f^*_{a} \alpha_{Q,a} (\chi'_{a} + i \chi''_{a}),$$

and the enhancement is given by:

$$|F_{Q,a}|^2 - |F_{Q}^{0}|^2 = F_{Q}^{0} \sum_{l} \Re(\alpha_{Q,l}) (2\Delta_{a} + \chi''_{a}) \rho_{Q} (\frac{r_{0}|\mathbf{M}_{Q,a}|^2}{\Gamma_{a}}/[\Delta_{a}^2 + \chi''_{a}^2 + \frac{1}{4}]) \frac{1 - n(E_a)}{F_{Q,a} - i f^*_{a} F_{Q}^{0} \rho_{Q} r_{0} b^2 c^2 / 2\pi E_{a}^2},$$

and

$$\ln(A_{E=E_a})_{k,T} = \ln(\mu_{0m,T}(1+X_{k,T})) = \ln(\mu_{0m,T}) \{1 + (X_{k,T} - \frac{1}{2} X_{k,T}^2 + \frac{1}{2} X_{k,T}^3 \ldots) / \ln(\mu_{0m,T})\}. \quad \text{(2.5)}$$

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

$$\Delta \varepsilon_{T,K} = \frac{e_{T,K}}{e_{T,C\,k-1}} = \ln(\frac{\mu_{0m,T}}{\mu_{0m,T1}}) / \ln(\frac{\mu_{0m,T1}}{\mu_{0m,121K}}) \times \ln(\frac{\mu_{0m,121K}}{\mu_{0m,T}}) \{1 + (X_{k,T} - X_{k,T1})(1 + 0^{\circ} \ldots) / \ln(\frac{\mu_{0m,T}}{\mu_{0m,T1}}) + (X_{k,121K} - X_{k,T1})(1 + 0^{\circ} \ldots) / \ln(\frac{\mu_{0m,121K}}{\mu_{0m,T1}})\} \quad \text{(2.6)}$$
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 \( |M_{Qa}|^2 \), when \( \varepsilon_0, \varepsilon_a \) 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 \( 121 K > T > 93 K \), indicates a mixture of phases is present, say:

\[
N(\text{normal metal})_{T > 121 K} \leftrightarrow M(\text{mixed})_{121 K < T < 93 K} \leftrightarrow SC_1(\text{superconducting})_{T < 93 K},
\]

where the mixed state absorbance (fig. 2e), and activity are the sum of contributions\(^{12w}\),

\[
\langle A_{E \geq \text{edge}, T} \rangle = \mu_{0m,T}(M) = x_{SC1} \mu_{0m(SC1)} + x_N \mu_{0m(N)}, \quad a = x_{SC1} a_{SC1} + x_N a_N,
\]

\( a = 1 \) for pure solids, and \( x_{SC1} \) is the mole fraction of the superconducting state in (3). Then:

\[
\exp(-\Delta G^f_{\geq 2}/k_B T) = (x_{SC1}/x_N)_{121 K < T < 93 K} = \frac{\langle A_{E \geq \text{edge}, T} \rangle - \langle A_{E \geq \text{edge}, 121 K} \rangle}{\langle A_{E \geq \text{edge}, T_{c1}} \rangle - \langle A_{E \geq \text{edge}, T} \rangle}
\]

obtains the standard state free enthalpy of formation, \( \Delta G^f_{\geq 2} \) at the two edges to better than 1% reproducibility (fig. 2f), indicating the involvement of the BaO layer chemical activity, by \( \Delta H^f_{\geq 2} = -220 \text{ meV} \) and \( \Delta S^f_{\geq 2} = -2 \text{ meV/K} \) and that energy and symmetry are gained in (3). This compares with energy necessary for the reported motion in YBa\(_2\)Cu\(_3\)O\(_{7-x}\), across \( T_c \) by anelastic relaxation time measurements, \( t = t_0 \exp(-W_i/k_B T) \) where \( (t_0, W_i) = (4E_{14}, 160\text{meV}) \) 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 CuO\(_2\) layer, at the phase transition that appears to be similar to the correlated and uncorrelated oxygen octahedral rotations in the parent compound, SrTiO\(_3\) at the 103 K phase transition\(^{2s}\), leaving an energy balance, \( W_i + \Delta H^f_{\geq 2} + 103k_B \approx -50 \text{ meV} \) to form a stable mixed state. Pauling describes the contribution to superconductivity in layer cuprates, by resonance between 2 pure Cu=O covalent bonds forming 90° to each other, or 4 half covalent and half ionic\(^{1l}\), which is equivalent to an electron density distribution in the Cu\(_4\)O\(_4\) highest occupied states (HOMO) obtained by self consistent field, SCF calculation for the CuO\(_2\) layer in a perfect cuprate lattice using MOTECC-91 codes (fig. 1b)\(^{1l}\), 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 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 SC₁ and SC₂ is indicated by the rise in Ab above Tc₁ (fig. 2e) where the mixture:

\[ SC₁(\text{superconducting})_{Tc₁<T<Tc₂} ⇔ SC₂(\text{superconducting})_{T<Tc₂=71.2K}, \]

is described by the Gibbs free enthalpy of formation:

\[ -\Delta G^\neq /k_B T = \ln(x_{SC₂}/(1-x_{SC₂}))_{Tc₁>Tc₂} = [A_{E_{\text{Edge},T}} - A_{E_{\text{Edge},Tc₁}}]/[A_{E_{\text{Edge},Tc₂} - A_{E_{\text{Edge},T}}}], \]

and indicates that the chemical activity is halved below Tc₁, \( \Delta H^\neq = -86 \text{ meV}, \Delta S^\neq = -1 \text{ meV/K} \) (fig. 2f), and that the mixture favors ordering.

Thus enhanced XAS/XRD measurements indicate that the Cu:(nd5/2,3/2), Ba:(nd5/2,3/2), O:(np1/2,3/2) and Y:(np1/2,3/2) electron density contribute significantly to E_HOMO and E_LUMO interactions near Tc, and that there is need for vacuum sites in YBa₂Cu₃O₇-\( \delta \) (insert fig. 1a) for \( e^2_2 \), periodic phonon interactions that lead to BCS type superconductivity[2v]. But, the motion is more complex in YBa₂Cu₃O₇-x, than in the parent SrTiO₃ perovskite due to barriers introduced by an incomplete oxygen octahedral crystal field. The role of \( |M_{Q,a}|^2 \) near Tc 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:

\[ |E_{\text{HOMO}}> ⇔ |E_{\text{LUMO}}>, \]

separated in energy by the shifts observed at say the Cu L₃,₂ Ea, of 0.4 eV (fig, 1a) across Tc.

**Conclusion**

Chemical activity in YBa₂Cu₃O₇-\( \delta \), 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**

Navacerrada, H Sahibudeen, KK Singh, C Chigvinadze, CT Lin and WY Liang ) is gratefully acknowledged.
Table I: YBa$_2$Cu$_3$O$_{7-δ}$ 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, $β_{[001]}=k_0^c$, and $φ_{[001]}=ε_{[001]}^a$ when $(π/2-k_0^cG_{[HKL]})−θ_{Bragg}$ 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 $f_0^l$ Cromer Mann Atomic Scattering Tables$^{[28]}$, obtain $θ(E_a)$ and $F_0^Q$ when the Bragg condition is satisfied for an XRD $[HKL]$ reflection plane.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>1</td>
<td>1</td>
<td>7</td>
<td>1</td>
<td>8</td>
<td>17</td>
<td>16</td>
<td>9</td>
<td>29</td>
<td>32</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>$Q_{[HKL]}$ (1/Å)</td>
<td>0.538</td>
<td>0.538</td>
<td>4.416</td>
<td>4.883</td>
<td>9.145</td>
<td>8.763</td>
<td>5.363</td>
<td>15.600</td>
<td>17.214</td>
<td>17.062</td>
<td>15.239</td>
<td>12.372</td>
</tr>
<tr>
<td>$D^0_{ac}$, $F_0^Q$</td>
<td>-5.9</td>
<td>-5.9</td>
<td>-45.4</td>
<td>-34.8</td>
<td>-29.0</td>
<td>-28.2</td>
<td>-33.6</td>
<td>30.0</td>
<td>39.2</td>
<td>33.7</td>
<td>24.6</td>
<td>2.2</td>
</tr>
<tr>
<td>measured $E_{ac}$ (eV)</td>
<td>540</td>
<td>924</td>
<td>5255</td>
<td>5627</td>
<td>9023</td>
<td>8990</td>
<td>8990</td>
<td>17047</td>
<td>17047</td>
<td>17047</td>
<td>17047</td>
<td>17047</td>
</tr>
<tr>
<td>$θ_{Bragg,Ea}$ (°)</td>
<td>79.37</td>
<td>35.06</td>
<td>56.01</td>
<td>58.89</td>
<td>74.09</td>
<td>36.06</td>
<td>64.54</td>
<td>85.06</td>
<td>60.66</td>
<td>61.89</td>
<td>45.73</td>
<td>89.51</td>
</tr>
<tr>
<td>Element Enhance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Σα_{ac}F_0^Q/</td>
<td>F_0^Q</td>
<td>^2=</td>
<td>-0.17</td>
<td>-0.17</td>
<td>0.01</td>
<td>0.06</td>
<td>-0.03</td>
<td>-0.04</td>
<td>-0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>$Σα_{ac}F_0^Q/</td>
<td>F_0^Q</td>
<td>^2=</td>
<td>-0.18</td>
<td>0.21</td>
<td>0.03</td>
<td>0.07</td>
<td>-0.03</td>
<td>0.03</td>
<td>0.07</td>
<td>-0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Σα_{ac}F_0^Q/</td>
<td>F_0^Q</td>
<td>^2=</td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>measured:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$β_{[001]}$ (°)</td>
<td>6.61</td>
<td>60.5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td>45</td>
<td>25</td>
<td>5</td>
<td>30</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>$φ_{[001]}$ (°)</td>
<td>0.0</td>
<td>0.0</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>$E_{Bragg}(β)$ (eV)</td>
<td>534</td>
<td>1078</td>
<td>5279</td>
<td>5627</td>
<td>9162</td>
<td>9139</td>
<td>8841</td>
<td>16983</td>
<td>17048</td>
<td>17160</td>
<td>16969</td>
<td>17263</td>
</tr>
<tr>
<td>$θ_{Bragg,Ea}(β,φ)$ (°)</td>
<td>83.39</td>
<td>29.50</td>
<td>55.62</td>
<td>58.89</td>
<td>29</td>
<td>37</td>
<td>71</td>
<td>85</td>
<td>45</td>
<td>60</td>
<td>62</td>
<td>45</td>
</tr>
<tr>
<td>$ε_{[003]}^G_{[110]} = -45^{(°)}$</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>10.1</td>
<td>19.5</td>
</tr>
<tr>
<td>$% Δθ_{Bragg}/θ$</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>$% ΔE_{Bragg}/E$</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 $α_{ac}Q_0^F/|F_0^Q|^2$ is observed when deviations $Δθ/θ$, and $ΔE/E$ 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 ($α_{Cu(1)} + 2α_{Cu(2)}$) $Q_0^F$ mostly cancel.

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

Figure 1: YBa$_2$Cu$_3$O$_{7-\delta}$ 30 nm film on SrTiO$_3$. (a) Temperature cycle of XRD I$_{[001]}$ reflection enhanced near the Cu L$_{3,2}$-E$_a$ ($\Delta$Q$_{[001]} \approx 0.01$ to 0.03 Å$^{-1}$) over 24 h in the JB Kortright chamber at DOE-LBL-ALS, indicates edge shifts of ~0.4 eV and intensity doubling below T$_c$ where a c-axis decrease below T$_c$ of 0.1% would propagate to a further decrease in $\Delta$0/0$_{Bragg}$ (Table I) and therefore I$_{[001]}$. Cartoon insert describes the layer stacking in the ideal D$_{4h}^1$ Space Group 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’ $\beta_{[001]}$. (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, describe the $\sigma$-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$_{7-\delta}$ Ba L$_{3,2}$-edge absorption, A enhanced by reciprocal scattering near T$_c$ at certain orientations: (a) Near edge absorbance, A(T, $\beta_{[001]}$) versus E$_a$, at different T near T$_c$ when $\beta_{[001]}=10\pm1^\circ$: 121 to 100K, 99 to 95 K, 93 to 92K, 88 to 70K, and 69 to 56K, and when $\beta_{[001]}=0$, and 5±1$^\circ$ respectively between T=121 to 56K A appear unchanged. (b) Ln(A$_E$/E$_a$)=ln($\mu_0$(1+X)) versus E>E$_a$. (c) Enhancement deviation (2.6) at $\beta =10^\circ$, $\Delta$e$_{k,T}$ =ln(A$_E$/A$_{93K}$)/ln(A$_{93K}$/A$_{121K}$)-1 versus |k|=\sqrt{(2me(E-E_edge)/\hbar^2)}. (d) Cartoons of layer orientation relative to incident, transmitted and scattered X-Rays, I$_{0j}=T_j$, T$_{0j+1}$, S$_j$ respectively. (e) Absorbance averaged over all k (230 data points at each T), <A>$_k$ versus 1/T near T$_c$ when $\beta_{[001]}=10\pm1^\circ$. (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$\geq$T$_{c1}$=92K: E>E$_{L3}$:*, E>E$_{L2}$:m, and for T$_{c1}$<T$\leq$T$_{c2}$=71K: E>E$_{L3}$:+, E>E$_{L2}$:x. For T$\geq$ 92K the fit accuracy, R$^2$=0.99 is better than for 92<T$\leq$ 71K, of R$^2$=0.93.

Figure 3: YBa$_2$Cu$_3$O$_{7-\delta}$ 30 nm film on SrTiO$_3$ for reversible temperature cycle near O K-E$_a$, $\Delta$Q$_{[001]} \approx$ -0.04 to 0.06 Å$^{-1}$. Sites’ are identified by the phase $\alpha_{Q,a}$ sign for the enhancement (Table I) in agreement with the literature. Changes in I$_{[001]}$ below T$_c$ suggest state occupation changes below T$_c$.

Figure 4: Single crystal CT-YBa$_2$Cu$_3$O$_{7-\delta}$ A. (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$_3$

Temperature Cycle

- Initial RT
- 4K
- Final RT

(a$^2$+b$^2$)$^{1/2}$ $\sum_j T_{j+1} = A$

$D_2^{1h}$

$F_0^{[001] \alpha_{CuO}} = -0.8$

$F_0^{[001] \alpha_{CuO_2}}$

$\Delta Q(1/{\AA}) = 2\pi[2 \sin(2\theta(65.5^\circ) - \theta(29.5^\circ))]/\lambda - 1/c$

Figure 1(b)

MO$_{74}$

$m=53,54$

$\varepsilon_m (H)$

$\varepsilon_m (H)$

$m=53,54$
Figure 2:

(a) $A_{BaL3}$

\[ \ln(A_{E2E_a\beta_{[001]}}) = \ln(<A_{E2E_a}>)+X-\frac{1}{2}X^2 \]

(b) $A_{BaL2}$

(c) $\Delta G^\neq/k_B = \frac{2531}{T} - 25$

(d) $\Delta G^\neq/k_B = \frac{2587}{T} - 26$

(e) $\Delta G^\neq/k_B = \frac{1247}{T} - 15$

(f) $\Delta G^\neq/k_B = \frac{773}{T} - 9.7$

\[ \sum_{j=1}^{10} T_j + 1 \Rightarrow A \]
Figure 3

$YBa_2Cu_3O_{7-\delta}$ 30nm film on [001]SrTiO$_3$

$Ib/I_0$ near O K-E, Temperature Cycle: --- Initial RT, - to 4K, — 44 K, - to RT

$\alpha_{O(CuO)} F_{[001]}^0 > 0$

$\alpha_{O(BaO)} F_{[001]}^0 < 0$

$\Delta Q = \frac{2\pi(2\sin(2\theta(162.4^o)) - \theta(83.39^o))/\lambda}{-1/c}$

0.015

0.01

0.005

0.001

0.0005

0.0001

0

-0.0001

-0.0002

-0.0003

-0.0004

-0.0005

-0.0006

-0.0007

-0.0008

-0.0009

-0.001

503 513 523 533 543 553 563 573 583 593

eV

0.015

0.01

0.005

0.001

0.0005

0.0001

0

-0.0001

-0.0002

-0.0003

-0.0004

-0.0005

-0.0006

-0.0007

-0.0008

-0.0009

-0.001

503 513 523 533 543 553 563 573 583 593

eV

-0.037
Figure 4:

(a) CT: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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

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

$\mu_0 m = 1.15$

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

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

$\frac{1.6}{1.15}$

$0.85$

$8.970 \ 9.015(\text{keV})$

$0.0 \ 1.6$

$9.015 \ 9.215$

$\text{atan}$

$0^\circ$

$1.5^C$

$0.03$

$-0.02$

$9.015(\text{keV})$