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Juana Vivó Acrivos, San Jose State University

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YBa$_2$Cu$_3$O$_7$ electro magneto-optic effects in Ba L$_{2,3}$ X-ray absorption near $T_c$

J.V. Acrivos,

*San Jose’ State University, One Washington Square, San José CA95192-0101*

jacrivos@athens.sjsu.edu, Tel: 408 924 4972; Fax 408 924 4945

running title: **YBa$_2$Cu$_3$O$_7$ magneto-optic effects near $T_c$**

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**Abstract**

The onset of electro magneto-optic effects, observed at the Ba L$_{2,3}$ edges synchrotron X-ray absorption by a YBa$_2$Cu$_3$O$_7$ single crystal, 10 K above the transition temperature to superconductivity, $T_c \sim 92$ K is used to identify the role played by the Ba donor layer in the transition to superconductivity in the CuO$_2$ layers. Negative permeability leads to Faraday rotation of the transmitted beam below $T = 112$ to 56 K for the 22 µm thick single crystal (c-axis orientation of $8\pi/18$ relative to $e_{X-rays}$) and sharp changes in the density of empty final states lead to zero transmitted radiation in an interval $\Delta E$ at the given orientation. The temperature dependence: $\Delta E(L_2) = 1.4$, 3.5 and 3.9 eV while $\Delta E(L_3) = 5.3$, 6 and 7 eV at $T = 92$, 74, 63 K respectively, indicates that the width of the empty final states bands increases as $T$ decreases. $\Delta E(L_3)/\Delta E(L_2) = 3.8$ at 92 K to 1.8 at 63 K, also indicates that the d$_{5/2}$ symmetry bands fill faster than those of d$_{3/2}$ symmetry below $T_c$, providing the first experimental evidence of unpaired spin-orbit states in the Ba donor layer of a superconductor. These effects, characteristic of ferromagnetic and anti-ferromagnetic materials near a resonance absorption, signal the onset of a Mott transition. The interaction between the layer states is described using 1D conjugate molecular orbitals.
1. Introduction

The purpose of this work is to determine how electro magneto-optic effects [1-5] if present in the layer superconductor YBa$_2$Cu$_3$O$_7$ (YBCO$_7$) (Fig. 1a,b) affect the onset of the transition to superconductivity, at temperature $T_c$ [6-11]. The electromagnetic properties of a metal are determined by an unbalance in the population of its spin-orbit split conduction band states. The X-ray absorption spectra, XAS at an element L$_{2,3}$ edges measure the transition probabilities for the excitations:

$$(1s)^2(2s)^2(2p_{1/2})^2(2p_{3/2})^4 \quad \Leftrightarrow \quad (1s)^2(2s)^2(2p_{1/2})(2p_{3/2})^4 \ldots (nd_{3/2}), \text{ at the element L}_2 \text{ edge}$$

$$(1s)^2(2s)^2(2p_{1/2})^2(2p_{3/2})^4 \quad \Leftrightarrow \quad (1s)^2(2s)^2(2p_{1/2})^2(2p_{3/2})^3 \ldots (nd_{5/2}), \text{ at the element L}_3 \text{ edge}.$$  

which are split, by spin orbit interactions in the core and in the conduction band state, i.e.,

$$\Delta E_{L_{2,3}} = h\nu_{L_2} - h\nu_{L_3} = \Delta E_{\text{final states}} - \Delta E_{\text{core}}.$$  

$\Delta E_{L_{2,3}}$ is dominated by the separation of core states, $-\Delta E_{\text{core}} \approx Z_{2p,\text{effective}}^4/32c^2$ Hartree is the relativistic textbook relation for hydrogen like core states [12a]. $Z_{2p,\text{effective}}$ is the 2p electron shielded atomic number ($\approx 24$ for Cu and $\approx 50$ for Ba is estimated from the L$_{2,3}$ edge separation when $\Delta E_{\text{final states}} << 1$) and $c$ is the velocity of light in atomic units. Recent work has shown that the XAS by a YBCO$_7$, 22 $\mu$m thick, single crystal at the Ba L$_{2,3}$ edges [6, 7] is enhanced below $T = 112$ K going from $e_{\text{axis}}^* e_{\text{X-ray}} = \pi/2$ to $8\pi/18$ for linearly polarized synchrotron X-rays (Fig. 2). Changes in the components of the index of refraction: $n = 1 - \delta - i\beta$ [text book relation 12b,c] produce a Faraday/Kerr rotation if $n_+$ and $n_-$ for the right and left the handed components of the incident linearly polarized radiation, are not equal due to electromagnetic interactions in the L$_{2,3}$ edge transitions final states [1, 2]. Since the population of the final states gives rise to the electromagnetic properties, and d-symmetry band states have been associated with superconductivity in YBCO$_7$, the Ba L$_{2,3}$ edge XAS data is used here to ascertain how changes in the $d_{5/2}$, $d_{3/2}$ symmetry empty final states, in the donor layer affect the CuO$_2$ conduction layer states near $T_c$. 

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2. Materials and Methods

The XAS of a 22 µm thick single crystal YBCO grown at the IRC for Superconductivity, Cavendish Laboratory [6, 7] were determined in transmission, T geometry (Fig. 1c) near the Ba L_{2,3} edges at the Stanford Radiation Laboratory, SSRL in the earth electromagnetic field. In order to evaluate the components of the complex index of refraction near T_c detailed orientation measurements are required at a synchrotron facility. These experiments report only the variation with temperature of the magneto-optical effects at a single orientation in order to identify how the final states and their occupation vary near T_c. The onset of superconductivity, was determined by the transparency induced by Abrikosov vortices at the Cu K-edge [6, 7, 11].

3. Results

The raw data, corrected only for a linear background subtraction gives the Absorbance for the single crystal at T = 112 K (Fig. 2, insert):

\[ A = \ln \left( \frac{I_T}{I_0} \right) / \ln(10) \]

in T geometry (Fig.1c). The ratio \( A(T)/A(121-112K) \) for T <112 K indicates up to a threefold enhancement as T decreases below T_c, at the orientation \( c^\wedge \varepsilon_{x-rays} = 8\pi/18 \). The temperature dependence of the interval \( \Delta E \) where the transmission vanishes, is indicated for the L_2 and L_3 edges respectively (Fig. 2 inserts).

4. Discussion:

The response components of the scattered or transmitted light I_s or I_T respectively from an incident linearly polarized beam, I_0 by atom a in YBCO (Fig. 1) are written [12 b,c]:

\[ f_a = f_a^0 + f_a^1 + i f_a^2. \]

(2)

The matrix elements leading to (2) are the square of the vector potential \( A^2 \) acting once on the electron number density \( \rho(r) \) to give \( f_a^0 \) responsible for Bragg diffraction far from an element
edge, and near an element edge the energy density $j \cdot A$ acts twice to give the anomalous Bragg diffraction: $f_a'$ (dispersion) and $f_a''$ (absorption), where $j$ is the current density. Electric and magnetic field $E$, $H$ rotations by $\phi_{\text{Kerr}}$ or $\phi_{\text{Faraday}}$ are observed in $I_s$ or $I_T$ for both ferromagnetic and antiferromagnetic materials[1, 2, 5]:

$$\phi_{\text{Kerr}} = -\Im \left[ \frac{n_+ - n_-}{n_+ + n_- - 1} \right] \quad \text{with ellipticity} \quad \varepsilon_{\text{Kerr}} = -\Re \left[ \frac{n_+ - n_-}{n_+ + n_- - 1} \right]$$

$$\phi_{\text{Faraday}} = \left[ \pi \frac{E z}{\hbar c} \Re \left( n_+ - n_- \right) \right] \quad \text{with ellipticity} \quad \varepsilon_{\text{Faraday}} = -\tanh \left[ \pi \frac{E z}{\hbar c} \Im \left( n_+ - n_- \right) \right]. \quad (3)$$

These give rise to an elliptical polarization of the scattered and transmitted beams respectively. A non zero ellipticity, is caused by unequal changes in the complex $n_+$ and $n_-$ versus photon energy, $E$, $\hbar$ is Planck constant and $z$ the distance traversed inside the sample. The final density of states at the $L_{2,3}$ edges, respectively is responsible for the changes in $\delta$ and the critical angle, ($2 \delta)^{1/2}$ for external reflection [textbook definition in ref. 12c] leads to sharp decreases/increases in the transmission over an interval $\Delta E$ (where the slope of the empty final density of states versus $E$ diverges, i.e., $d\delta/dE \Rightarrow \pm \infty$). The limits determined by $\Delta E$ indicate where sharp changes occur in the density of empty final states, related to the $L_2$ and $L_3$ band widths. For 20 to 60 nm Fe ferromagnetic films [Fig. 8 ref. 5] $\Delta E(L_3) \sim 2$ eV and $\Delta E(L_2) \sim 0.28$ eV indicate that the empty states band width is 7.2 times greater for $3d_{5/2}$ than for $3d_{3/2}$, suggesting that the latter is the majority occupied band. The experimental results are discussed in three parts:

A. The 22 $\mu$m YBCO$_7$ crystal electromagnetic properties determined by Ba $L_{2,3}$ XAS are:

(i) The sharp changes in the index of refraction in the interval $\Delta E$, observed below 112 K, $\Delta E(L_3)/\Delta E(L_2)$ =3.8 at 92 K to 1.7 at 63 K (Fig. 2 Table insert) indicate that the relative widths and/or population of the $d_{5/2}$ and $d_{3/2}$ symmetry final empty states bands have a different temperature dependence which result in different electromagnetic properties versus $T$. 

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(ii) The ratio $\Delta E(L_3)/\Delta E(L_2) = 3.8$ near $T_c$ is smaller than that for a ferromagnetic Fe film of 7.2 [8] at room temperature indicating a greater unbalance of spin-orbit states and therefore stronger magnetic properties for the latter. The unequal population of $d_{5/2}$ and $d_{3/2}$ symmetry final states does not distinguish between ferromagnetic and antiferromagnetic properties, but an equal probability for their occupation should obtain $\Delta E(L_3)/\Delta E(L_2) = 1.5$.

(iii) Faraday rotation extends into the extended X-ray absorption, XAFS as indicated by the enhanced absorption over that at 121 K (Fig. 2).

(iv) The unpaired spin states in the donor layer may be the cause and/or consequence of spin defects in the CuO$_2$ conduction layer states, that can lead to the formation of superconducting pairs at the onset of superconductivity described as follows.

B. The molecular orbital, MO description of the material suggested by the data is:

(i) The wave functions [12a] involved in the transitions are:

**Ba initial core states:**

$\psi_{\text{Ba},i}^{2p_{3/2}}$: $|3/2,\pm3/2> = Y_{1,\pm1}^{↑↓}R_{2,1}(r_{\text{Ba}})$, $|3/2,\pm1/2> = 3^{-1/2}[2^{-1/2}Y_{1,0}^{↑↓} \pm Y_{1,\pm1}^{↑↓}]R_{2,1}(r_{\text{Ba}})$

$\psi_{\text{Ba},i}^{2p_{1/2}}$: $|1/2,\pm1/2> = 3^{-1/2}[Y_{1,0}^{↑↓} - 2^{1/2}Y_{1,\pm1}^{↑↓}]R_{2,1}(r_{\text{Ba}})$

and empty final band states band containing fractional character of:

$\psi_{\text{Ba},f}^{5d_{5/2}}$: $|5/2,\pm5/2> = Y_{2,\pm2}^{↑↓}R_{5,2}(r_{\text{Ba}})$, $|5/2,\pm3/2> = 5^{-1/2}[2Y_{2,\pm2}^{↑↓} \pm 2Y_{2,\pm1}^{↑↓}]R_{5,2}(r_{\text{Ba}})$, $|5/2,\pm1/2> = 15^{-1/2}[3^{-1/2}Y_{2,0}^{↑↓} \pm 6^{1/2}Y_{2,\pm1}^{↑↓}]R_{5,2}(r_{\text{Ba}})$

$\psi_{\text{Ba},f}^{5d_{3/2}}$: $|3/2,\pm3/2> = 5^{-1/2}[2Y_{2,\pm2}^{↑↓}-Y_{2,\pm1}^{↑↓}]R_{5,2}(r_{\text{Ba}})$, $|3/2,\pm1/2> = 15^{-1/2}[6^{1/2}Y_{2,0}^{↑↓} - 3Y_{2,\pm1}^{↑↓}]R_{5,2}(r_{\text{Ba}})$

where $Y_{l,n}(r_{a},\theta_{a},\phi_{a})$ are spherical harmonics, the sub indexes $↑↓$ represent the spin $s_z = \pm1/2$ states and $R_{n,l}(r_{a})$ is the radial dependence when $(r_{a},\theta_{a},\phi_{a})$ are the spherical polar coordinates of the electron relative to atom $a$. The LCAO-MO extended state wave functions for the [CuO$_2$]$_n$ conduction layer, obtained by a SCF analysis give the maps of electron density, $\rho_c > (0.1/\text{bohr})^3$. 5
indicating the direction of the extended electron overlap population along O\(_{3a}:2p_{ab}\)-O\(_{3b}:2p_{ab}\) the a,b and a,-b diagonals (Fig. 3 a,b) [13]. These are built with SCF, MO: \(\chi_{m,M} = \chi_{m,74}(Cu_4O_4)\) and \(\chi_{m',114}(Cu_4O_{12})^x\) (M is the total number of doubly occupied MO and m is the order of increasing energy, \(\varepsilon_{m,M}\)) where the \(\chi_{m,74}\) are doubly degenerate with an overlap population along the ab or a,-b diagonal (Fig. 3a, e.g., m = 53/54, 63,64, etc.). The highest occupied SCF MO, HOMO \(\rho_c\) (m =74/75) identifies the direction of electron overlap population at the Fermi level that agrees with the preferred direction of superconductivity along the a,b and a,-b diagonals, determined experimentally by photoemission measurements [14] later. The experimental conduction electron state wave vectors in the first Brillouin Zone, \(k_\pm = (k_y, k_x, k_z) = \pm (\pi, \pm \pi, 0)\) are used in a semi empirical tight binding approximation [12 g] of the layers.

(iii) The extended states are usually built with \(k_\pm\) and the SCF MO basis [13] (Fig. 3c).

Here simple Alternant 1D conjugate orbitals [15] in a lattice with atom coordinates (Fig. 1a,b, 4):

\[
R_{Cu}: (x/a, y/b, z/c) = (n+n_a, n+n_b, 0),
\]

\[
R_{O3a}: (n+n_a+\frac{1}{2}, n+n_b, \delta)\] and \(R_{O3b}: (n+n_a, n+n_b-\frac{1}{2}, 0.02)\)

and donor layers \(R_{Ba,Y}: (n+n_b + \frac{1}{2}, n+n_b- \frac{1}{2}, 0.16)\)

are used. \(n_a, n_b = 0, 1, \text{ etc.}\) identify the chains, \(n = 0, 1, .N.\) \(k_+ = \pm(\pi, \pi, 0)\) obtains the MO:

\[
\chi_{O, na,nb} (r, \pi, \pi, k_z) = (2N)^{-\frac{1}{2}} i \cos(\pi(n_a + n_b)) \sum_n [\psi_O(r-R_{O3a}) - \psi_O(r-R_{O3b})],
\]

\[
\chi_{Cu, na,nb} (r, \pi, \pi, 0) = N^{\frac{1}{2}} \cos(\pi(n_a + n_b)) \sum_n \psi_{Cu}(r-R_{Cu}),
\]

\[
\chi_{donor, na,nb} (r, \pi, \pi, k_z) = N^{\frac{1}{2}} \cos(\pi(n_a + n_b)) \sum_n \psi_{donor}(r-R_{donor}).
\] (5)

\(N\) is the total number of Cu sites in a chain and \(\psi\) are atomic orbitals. Along the a,-b diagonal, the 1D overlap occurs for \(k_\pi = \pm (\pi, -\pi, 0)\). However, if \(k_\pi\) changes to \(k_\phi\) the O\(_{3a}:2p_{ab}\)-O\(_{3b}:2p_{ab}\) 1D overlap changes direction (Fig. 3c, 4a, b) creating anti-bonding states, which in turn give rise to periodic lattice distortions, PLD.
(iv) A periodic repeat between broken bonds (Fig. 4) creates expansion and compression waves that can be detected by X-ray diffraction, XRD. A 1D PLD with \( \lambda_{\text{PLD}} = 12 \) a has been observed in a 50 nm YBCO\(_7\) film [\( a = 4.88 \) Å in ref. 10] but 4 by 4 PLD can also be explained by the interchange of \( k_+ \) changes to \( k_- \) (Fig. 3c). The undistorted 1D chain length determines the conduction electron mean free path in the chain, and the defect unpaired spin states may be the cause and/or the result of the magneto-optic property changes in the Ba donor layer 10 K before the onset to superconductivity. The energy cost for breaking a \( O_{3a:2p_{ab}-O3b:2p_{ab}} \) bond is estimated from the SCF, LCAO-MO analysis. The difference in \( \rho_e \) between \( \chi_{54,74} \) and \( \chi_{57,74} \) is due to subtle changes in the \( O_{3a:2p_{ab}-O3b:2p_{ab}} \) overlap population (Fig. 3a). An additional resonance energy, \( t \) due to \( O_{3a:2p_{ab}-O3b:2p_{ab}} \) overlap is possible for \( \chi_{54,74} \) but not for \( \chi_{57,74} \) and obtains \( \epsilon_{57,74} - \epsilon_{54,74} = 0.16 \) eV \( \approx 2 \) t [13]. Also the SCF energy difference \( (\epsilon_{75,74} - \epsilon_{74,74})/2 = 0.95 \) eV between the \( Cu_4O_4 \) HOMO and LUMO is due to the difference in \( \rho_e \) for \( \chi_{74,74} \) and \( \chi_{75,74} \): Two \( Cu:p \)-like in the HOMO \( \rho_e \) symmetry are associated with a \( d^{10} \) closed shell, but addition of an electron gives two \( Cu:d \)-like in the LUMO \( \rho_e \) symmetry, associated with an open \( d \) shell. This is in agreement with the higher heat of formation per mole for the \( 3d^8 \) shell oxide, NiO over that for a \( 3d^{10} \) closed shell oxide, ZnO by 1.2 eV [12f]. The presence of broken \( O_{3a:2p_{ab}-O3b:2p_{ab}} \) bond defects does not necessarily increase the ground state energy because of the degeneracy introduced by, e.g., \( \chi_{54/53,74}, \chi_{57/56,74}, \chi_{64/63,74}, \chi_{66/67,74}, \chi_{74/75,74} \) (Fig. 3a) [13, 17]. This suggests that PLD are formed when \( k_- \) and \( k_+ \) are interchanged by an excitation of \( 2t/N \approx 0.16 \) eV/N when one \( O_{3a:2p_{ab}:O3b:2p_{ab}} \) becomes anti-bonding, in a chain of \( N \) atoms [15]. These excitations may be introduced at the onset of YBCO\(_7\) Ba lattice vibrations at \( T < 130 \) K [16], i.e., the YBCO\(_7\) 50 nm film (\( \lambda_{\text{PLD}}/a = 12 \)) would require excitations of 10 meV to change the spin state population.
(v) Electron pair states with \( J = 0 \), obeying Bose statistics can be formed by the interaction of an O:2p\(_{3/2}\) spin defect chain with another of Cu:3d\(_{3/2}\) symmetry (and/or Ba:5d\(_{3/2}\)). The two electron pair states are eigenfunctions of \( J = J_1 + J_2 \) and \( J_z \) but not \( S_z \). The parity of the product states, \( P \) for the exchange operation \( P_{12} \) of electrons 1 and 2 of \( d_{3/2} \) (Cu or Ba) and \( p_{3/2} \) (O) orbital symmetry give the allowed \(|J,0>\):

\[
\begin{array}{c|c|c|c|c}
|J,J_z> & \text{Matrix Coefficients} & d_{3/2} & p_{3/2} & P \\
\hline
|3,0> & 1/40^{1/2} [1 1 3 3] & (I+e^{iP_{12}}) & |3/2 1/2> & d_1* |3/2 -1/2> & p_2 \times 2\pi \\
|2,0> & 1/8^{1/2} [ -1 -1 1 1] & (I+e^{iP_{12}}) & |3/2 -1/2> & d_1* |3/2 1/2> & p_2 \times \pi \\
|1,0> & 1/40^{1/2} [ 3 3 -1 -1] & (I+e^{iP_{12}}) & |3/2 3/2> & d_1* |3/2 -3/2> & p_2 \times 2\pi \\
|0,0> & 1/8^{1/2} [1 -1 1 -1] & (I+e^{iP_{12}}) & |3/2 -3/2> & d_1* |3/2 3/2> & p_2 \times 2\pi \\
\end{array}
\]

(6)

where the matrix coefficients are obtained to satisfy the eigenvalues, \( J(J+1) \), \( J_z \), and the raising and lowering angular momentum textbook operations [12a]. \( I \) is the identity operation and electrons 1 and 2 are identified by the position in the product. The principal axis of quantization in relation (4) is determined by \( k_\pm \) and the electron pair \( e_2^- \) states allowed by symmetry in (6) are:

\[
|0,0>_{ab\ \text{chain}} = 5^{1/2} (I+ P_{12}) \{(Y_{1,0}^\uparrow \sum R_{O:2p}(r-R_{O3a}) - R_{O:2p}(r-R_{O3b}))|1* (Y_{2,0}^\downarrow \sum R_{Cu:3d}(r-R_{Cu}))|2 - (Y_{1,0}^\downarrow \sum R_{O:2p}(r-R_{O3a}) - R_{O:2p}(r-R_{O3b}))|1* (Y_{2,0}^\uparrow \sum R_{Cu:3d}(r-R_{Cu}))|2 \}
\]

(7)

for \( J = 0 \). Bose pairs arising from interactions between electron states in neighboring 1D chains along the diagonal a,b (Fig. 4) mediated by lattice vibrations in YBCO\(_7\) of \( \sim 10 \) to 80 meV [16b] are possible for \( J = 3, 1, 0 \) in (6).

(vi) Equal superconducting properties along the a:b and a:-b diagonals, in a perfect lattice may occur only in a crystal with \( k_+ \) and \( k_- \) quantization in two different CuO\(_2\) layers (e.g., YBCO\(_7\) Fig. 1a) or when an equal probability of \( k_+ \) and \( k_- \) quantization gives rise to bonding \( \leftrightarrow \) anti-bonding excitations of \( 2t/N \sim 6 \) meV, causing the commonly observed PLD.
C. Evidence for magneto-optic effects below $T_c$ has also been obtained in the enhanced 001 scattering by a 50 nm YBCO$_7$ film on SrTiO$_3$ with a 24 DEG grain boundary [8]. Near the Cu L$_{2,3}$ edges both the raw data $I_s/I_0$ and $f'$ (obtained from the raw data by an inverse Kerr rotation by $\phi_K =23.5$ DEG) indicate below $T_c$ a decrease in the final empty band states contribution of Cu:3d$_{3/2}$ symmetry (L$_2$ edge) that is greater than for the Cu:3d$_{5/2}$ contribution to the empty final states (L$_3$ edge) (Fig. 5a). Changes at the O K-edge are difficult to measure because the spin-orbit splitting in the final states bands is negligible (Fig. 5b). However in a film with grain boundaries, electron states are also introduced by broken bonds at the grain boundary in the same manner as when $k_+$ changes to $k_-$ (Fig. 4).

5. Conclusions

The temperature dependence of the YBCO$_7$, Ba L$_{2,3}$ XAS indicate that the onset of anti-ferromagnetic optic effects in the Ba layer $\sim$ 10 the K above $T_c$ forecasts the Mott transition [18] associated with the transition to superconductivity. The valence of an alkaline earth metal changes near the metal insulator Mott transition in Sr(NH$_3$)$_x$ as determined by XAS valence edge shifts [19]. The elegant work of Zhang et al. [20] helps to unravel the YBCO$_7$ superconductivity-magnetism relation. They have shown that spin polarized transport is non-dissipating and that transport by a Bose condensate in the superconducting state is a sub-group of spin polarized transport. A question remains: are the spin polarized nd$_{3/2}$ over the nd$_{5/2}$ band states in YBCO$_7$ a result of the Bose condensation, or does the uneven spin population in nearly 1D conjugate orbitals (5) cause the Bose condensation? Since Faraday rotations are observed above $T_c$, the latter appears closer to the truth.

6. Acknowledgements

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7. References


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8. List of Figures

Fig. 1: Schematic of sample and measurement parameters: (a) YBCO$_7$ crystal structure. (b) CuO$_2$ conduction layer intercalated between Ba and Y donor layers. (c) Scattered, $I_s$ and transmitted, $I_T$ beams of incident radiation, $I_0$ by sample. $I_s/I_0$ and $I_T/I_0$ measure the change in the initial state $|k,g>$ produced by complicated reflection and transmission operators $R$ and $T$ [ref. 1-5, 12]. $\theta = c^\epsilon_{\text{X-rays}} = 8\pi/18$ and $\theta = = k_i^a$ where $k_i$ is the direction of incident X-rays and $\epsilon_{\text{X-rays}}$ the direction of their linear polarization and $g$ represents the quantum state of the system.

Fig. 2: Ba L$_{2,3}$ edge XAS for YBCO$_7$ single crystal. $A(T)/A(121 \text{ K})$ at the orientation $\theta = 8\pi/18$ near $T_c$ of YBCO single Crystal of 22 $\mu$m thick [ref. 6,7]. The raw data is corrected only for baseline (indicated in insert). The ratio $A(T)/A(121 \text{ K})$ eliminates the effect of sample thickness, except for the magneto-optic effects. $A(T)/A(121 \text{ K})$ does not change appreciably from room temperature to 56K at $\theta = \pi/2$, but at $\theta = 8\pi/18$ the complex index of refraction indicates the presence of magneto-optic effects 10 K above $T_c$. The transmission (Fig. 1c) vanishes in the interval $\Delta E$ near the indicated resonance absorptions, and depend on $T$ (inserts).

Fig. 3: (CuO$_2$)$_n$ electron density contours of $\rho > 10^{-3}$/bohr$^3$ obtained for a $T'$-Nd$_2$CuO$_4$ nano-particle in the field of 18 unit cells [13]: (a) Cu$_4$O$_4$: $\chi_{m,74}$ (b) Cu$_4$O$_{12}$: $\chi_{m',114}$ (c) Tight binding SCF-MO approximation for $k_+ = (\pi, \pi, 0)$:

$$\Psi_{m'm}(r, k) = N^{1/2} \sum_R \{ \exp(i k'R_{74}) \chi_{m,74}(r-R_{74}) + \exp(i k'R_{114}) \chi_{m',114}(r-R_{114}) \} =$$

$$\Psi_{m'm}(r, (\pm \pi, \pm \pi, 0)) = 1/\sqrt{N} \sum_R \{ \chi_{m,74} (r-R_{74}) + \chi_{m',114} (r-R_{114}) \},$$

$n = 0, 1, ..., N/2$ and the MO are centered at: $R_{114} = 2n(a \pm b)$ and $R_{74} = 2(n a \pm (n-1) b)$.

Fig. 4: Direction of extended orbital overlap population in conjugate MO in the CuO$_2$ plane for $k_4$. The O$_{3a}$:2p$_{ab}$-O3b:2p$_{ab}$ overlap is indicated by solid lines (for + 2p orbital phase) and dashed lines (for - 2p orbital phase). The Cu:3d phase is indicated by solid lines (+ ) and dashed...
lines (-) respectively. Anti-bonding states are created where \( k_+ \) changes to \( k_- \) (blank). The PLD periodicity is produced by the repeat chevron symmetry.

**Fig. 5:** Enhanced 001 scattering by 50 nm YBCO\(_7\), film on SrTiO\(_3\) with a 24 DEG grain boundary according to ref. 8: (a) \( f' \) near the Cu L\(_{2,3}\) edges at different \( T \) above and below \( T_c \). (b) \( f'' \) near the O K edge at different \( T \) above and below \( T_c \).
Figure 1a:

Figure 1b:

Figure 1c:

\[ |k,g\rangle = l_0 + \text{Sample} \]

\[ a, b\text{-axes} \]

\[ YBCO \]

\[ |k,g\rangle = R_{g''g'}|k,g\rangle \quad \text{sample x} \]

\[ |k,g\rangle = T_{g'g}|k,g\rangle \]

\[ = l_s + \text{Sample} \quad = l_t + \text{Sample} \]
YBCO Ba L$_{2,3}$ Edge XAS: $\theta=8\pi/18$

Table of Extinction Interval

<table>
<thead>
<tr>
<th>T(K)</th>
<th>92</th>
<th>74</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (L$_3$)</td>
<td>5.3</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>$\Delta E$ (L$_2$)</td>
<td>1.4</td>
<td>3.5</td>
<td>3.9</td>
</tr>
</tbody>
</table>

$\Delta E$ (L$_3$)/$\Delta E$ (L$_2$) = 3.8  1.7  1.8

$195(121 - 112$ K$)$

Ln(I$_0$/I$_T$) $-4.1 10^{-3}-23.184$

$\Delta E$ (eV)

<table>
<thead>
<tr>
<th>E (keV)</th>
<th>5.247 E (keV)</th>
<th>5.257</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.25</td>
<td>5.35</td>
<td>5.55</td>
</tr>
<tr>
<td>5.65</td>
<td>5.75</td>
<td>5.85</td>
</tr>
</tbody>
</table>

$15$
Figure 3a:
Figure 3b:

\[ \rho_e > (0.1/b)^3 \]

\[ 1/4\{113,113\} \]

\[ 1/4\{114,114\} \]

\[ 1/4\{84,114\} \]

\[ 1/4\{101,114\} \]

\[ \text{Cu}_4\text{O}_{12}: \text{114 MO occupied} \]
Figure 3c:

Unit Cell
$\text{(CuO}_2\text{)}_{16}$

4 by 4 PLD

$2t_{114-114}$

$2t_{114-114}$

resonance

$\rho_e$

delocalized
Figure 4:

$(\pi, \pi) = (k_x, k_y) = (-\pi, \pi)$

$(\pi, \pi) = (k_x, k_y) = (\pi, \pi)$

$(\pi, \pi) = (k_x, k_y) = (-\pi, \pi)$
Fig. 5a:
Enhanced 001 Scattering by YBCO$_7$ 50 nm film on SrTiO$_3$, with 24 Deg GB: Anomalous Bragg Effect

\[ a: Cu_{L2,3} \text{ Edges vs } T \]

\[ \frac{f''}{f} \text{ from } L_s/L_0 \]

---

Fig. 5b:
Enhanced 001 Scattering by YBCO$_7$ 50 nm film on SrTiO$_3$, with 24 Deg GB: Anomalous Bragg Effect

\[ b: O K \text{ edge vs } T \]

\[ \frac{f''}{f} \text{ from } L_s/L_0 \]