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Spectroscopic evidence for polarons in partially occupied spin-orbit states of YBa$_2$Cu$_3$O$_7$

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The spin-orbit split white line, synchrotron X-ray spectra at the respective Cu and Ba L$_{2,3}$ and Ba M$_{4,5}$ edges in YBa$_2$Cu$_3$O$_7$ crystal, powders, films and derivatives are compared to those for standard BaBr$_2$ and CuO powders. The white line absorption integrated intensity, $I$ ratios: $r_{3,2} = I(L_3)/I(L_2)$ and $r_{5,4} = I(M_5)/I(M_4)$ for BaBr$_2$ are equal to the ratio of core states degeneracy, but $r_{3,2}$(Ba in YBCO powder) $< 2 < r_{3,2}$(Cu in CuO and YBCO film) and $r_{5,4}$(Ba in YBCO film) $< 1.5$ (Table I) indicate an apparent overpopulation of the Cu:3d$^{3/2}$ final states relative to the 3d$^{5/2}$, and the Ba:5d$^{5/2}$ over the 5d$^{3/2}$, and the 4f$^{7/2}$ over the 4f$^{5/2}$ at room temperature. The difference spectrum $DEL=A$(YBCO)−$A$(CuO) with a leading sharp peak, (HWHH of 0.2 eV) at $E_0+0.5\pm0.1$eV and the temperature changes in the atomic X-ray absorption fine structure A-XAFS observed at 0.08 to 0.07 nm near the heaviest atom, Ba suggest that charge polarization contributes to the final state band occupancy in YBCO.

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INTRODUCTION

The synchrotron X-ray absorption spectra (XAS) of layered cuprates, where superconducting planes are intercalated between ionic and perhaps magnetic layers in YBa$_2$Cu$_3$O$_7$ and its derivatives (YBCO) are compared to the CuO and BaBr$_2$ powder spectra at the Cu and Ba L$_{2,3}$ edges and the Ba M$_{4,5}$ edges for the purpose to ascertain evidence of charge polarization in YBCO.

EXPERIMENTAL

The samples are single crystals/powders grown at the Cavendish Laboratory$^1$ and 50 nm films that have mixed ab axes, grown epitaxially by sputtering in an oxygen atmosphere onto SrTiO$_3$, single crystal, (SC) and, bi-crystals (BC) with a 24 DEG ab grain boundary at the Complutense$^2$. XAS in transmittance (IT), in fluorescence (F) and total electron yield (TEY) were measured versus energy, $E$ calibrated at SSRL station 2-3 relative to Cu film Cu:K-edge, and at the LBNL-ALS 6.3.1 Nachimuthu chamber relative to CuO. Cu:L$_3$ edge$^6$. XAS, $A = \ln(I_0/I_T)$, (F/I$_0$), (TEY/I$_0$) when I$_0$ is the incident intensity and white line (WL) spin-orbit split transitions and WL integrated intensities, I are reported (Table I, FIG. 1 to 4).

FIG. 1 (b) YBCO single crystal where insert shows structure in $\Delta$ decreasing below $T_c$.

FIG. 1 Ba L$_{2,3}$: $A$, WL = $A$−$A_{\text{core to cont.}}$ Gaussian, $G$, shape fit to $WL$($E<E_0$), $\Delta = WL-G$, $I$

(a) KKD powder: ($Nd_{1.1}Ba_{1.9}Cu_3O_7$) insert shows $\Delta$ at $L_2$ and $L_1$ edges.

FIG. 2: YBCO film ($\epsilon_{\text{Film}}\epsilon_{\text{rays}}=\pi/4$) compared to CuO powder, WL at the Cu L$_{2,3}$ edge: $E_0$(Cu:L$_3$) = 931.2 eV, $A$=$A_{\text{YBCO}}$−$A_{\text{CuO}}$ (A normalized to $L_3$ amplitude maximum). Inserts show fit of sum $G$ shape peaks (HWHH=0.45eV) to $A_{\text{CuO}}$ with less than 2% error and to $\Delta$ with less than 1% error if an exciton peak is included.
Mass attenuation due to sample absorption at the two spin orbit split WL, determined by atomic cross sections differs by less than 8% in F, and is negligible in TEY and E > 10³ eV. The WL spectra are obtained by subtracting from A the background baseline (BL) and the extended X-ray absorption fine structure, XAFS origin region (FIG. 1), except where the XAFS contribution from the previous edge is less than 2% at the Cu:L2 and Ba:M4 edges in both YBCO and CuO (FIG. 2, 3).

RESULTS/DISCUSSION

The normalized A difference spectrum $\Delta A_{YBCO}-A_{CuO}$ gives information of interdependent effects on the states near the Fermi energy in YBCO, e.g., crystal field symmetry different from CuO, polarization effects9, and electron density in

![FIG. 3: WL at the Ba:M4,5 edges for YBCO film (c_film = $\varepsilon_{Crays} = \pi/4$) and BaBr2 powder. Weak shoulders in A BaBr2 are due to Br(L)~1.599, Br(L)~1.533 keV absorption from beam 2nd order harmonic. 3rd order harmonic (Nb(L)~2.3705 keV), is absent.](image)

![FIG. 4: Change in atomic XAFS versus T, XTDAS for YBa2Cu3O7- single crystal at Ba L2 edge through $T_c$. The XTDAS measures the changes in XAFS scattering amplitude [ref.4, 5, 11]: $\Delta(k) = 2 \sin(2kR_j + \phi(k))F(k,R_j)/kR_j$ caused by changes in the number density $N_j$ at $R_j$ with scattering amplitude $F$. When inter-atomic distances do not change across $T_c$, their contributions to $\Delta(k)$ cancel out in the XTDAS [ref.4, 5], and the appearance of a short wave oscillation, $\Delta k = 4 \pi^2$ indicates $N_j$ dependence at $R_j$ (FIG. 3). (a) Increase in $N_j$ across $T_c$ when $\varepsilon_{Crays}$ is in ab plane. (b) Decrease in $N_j$ across $T_c$ when $\varepsilon_{Crays}$ is out of ab plane.](image)

![FIG. 5: Highest occupied MO showing the electron density, $\rho_e$ continuous along O:2p_dz, diagrams, but discrete at Cu atom that can contribute to both polarization and periodic lattice distortions (PLD), and absorption through shake-up at $\sim E_F + 8eV$ at the Cu, Ba L2,3 edges: (a) Contours of $\rho_e \geq 10^{-3}b^{-1}$, $\varepsilon = 7000 eV$, $\varepsilon = 87.7, 86$, $\varepsilon = 30.8$, $\varepsilon = 78.5$, $\varepsilon = 78$, $\varepsilon = 92.3$, $\varepsilon = 98$ from CuO, polarization effects9, and electron density in YBCO, Ba are detected by the XAS temperature difference spectra relative intensity as follows: The XAS white lines (WL) show the electron density, $\rho_e$ near the heaviest element in YBCO, Ba are detected by the XAS temperature difference spectra, XTDAS amplitude versus k(bohr$^{-1}$) = (2(E-E_F)H$^{1/2}$) (FIG. 4). The observed oscillations identify a change in $\rho_e$ near $\sim 0.7$ to $0.08 eV$ from the Ba atom, across the transition to superconductivity, $T_c$ that reverses sign when the polarized synchrotron electric field, $\varepsilon_{Crays}$ is rotated out of the crystal ab plane. This indicates that the polarons of radius $r_p$ are involved.](image)
the core states degeneracy: $r_{3,2} = \frac{I(L_3)}{I(L_2)} = 2$ and $r_{5,4} = \frac{I(M_5)}{I(M_4)} = \frac{3}{2}$ (Fig. 3 and Table I). At the Cu L$_{2,3}$ edges: splitting$^8$: The WL separation, $\Delta E(\text{Cu:}L_{2,3}) = 19.7$ eV (Fig. 2) is the same as in other Cu compounds$^8$ though the crystal field induced structure depends on the 3$d^0$ filled Cu oxidation states$^{46}$. Crystal field split peaks appear from $E_0 + 10$ to $E_0 + 8$eV in Cu metal, partially oxidized Cu film and Cu quantum dots respectively$^9$, but the 10% asorbance present at $E_0 + 7$eV for both YBCO and CuO suggests that they have the same oxidation state Cu$^{2-3}:3d^0$ in a distorted lattice. Their difference spectrum $\Delta = \Delta_{\text{YBCO-CuO}}$ vanishes to within less than 1% for $E < E_0$ at the Cu(L$_{2,3}$) edges but differs by as much as 20% WL$_{\text{max}}$ for $E > E_0$ (insert Fig. 2) and may be described by a sharp (HWHH$\sim 0.2$eV) G shaped leading peak at $E_0 + 0.5 \pm 0.1$eV distinct from broader ones (HWHH$\sim 0.45$eV) at $E_0 \pm 1 \pm 7$eV (Fig. 2 insert). The first is too sharp to be assigned to a crystal field peak, the broader ones may be due to Cu$^{2-3}:3d^0$ crystal field shift lines if the oxidation state is present in YBCO, and/or XAS shake-up processes from CuO$_2$ layer MO orbitals below the edge by that amount (Fig. 5)$^{10}$. The Cu$^{3-}:3d^0$ should be similar to Ni$^{2+}$ WL spectra at the L$_{2,3}$ edges where all the cubic crystal field split lines show comparable amplitudes$^9$ while the Cu$^{3-}:3d^0$ splitting is reported to be twice as large$^{8b}$ as for Ni$^{2+}$. The source of the amplitude $\Delta$ appears to be due to charge polarization in the highest filled MO (Fig. 5) that in turn governs the crystal field symmetry.

At the Ba edges the WL can be fitted to G shapes (HWHH$\sim 2.5$eV) for $E < E_0$, with $\Delta E(\text{Ba:}L_{2,3}) = 376.2$eV and $\Delta E(\text{Ba:}M_{4,5}) = 14.0$eV for YBCO and BaBr$_2$ (Fig. 1, 3). The difference spectrum $\Delta = \Delta_{\text{YBCO-BaBr}}$G for $E > E_0$ is orientation dependent with amplitudes 30% WL$_{\text{max}}$ for $\varepsilon_{\text{X-rays}}$ in the ab plane that reduces to less than 10% of WL$_{\text{max}}$ when $\varepsilon_{\text{X-rays}}$ is rotated out of the ab plane by $\pm \pi/18$. For $\varepsilon_{\text{X-rays}}$ in the ab plane $\Delta$ shows a structure with a sharp leading peak similar to that observed at the Cu:Li edge (Fig. 1b).

The 2p effective atomic number is obtained in the hydrogen-like approximation$^8$ from $\Delta E$ (Table I) where the Pauling rules indicate that the Cu:2p electron nuclear charge is shielded by $\sim 1s^22s$ shells, the Ba:2p by $\sim 1s^2$ shells and the Ba:3d by $\sim 1s^22s^22p^3$ shells.

(iii) The final band state population, the crystal field and orientation in $\varepsilon_{\text{X-rays}}$ determines the WL transition probability$^5$. All orientations in $\varepsilon_{\text{X-rays}}$ are sampled in powders, and when all the accessible final states are empty in the ionic reference BaBr$_2$, the ratio of spin-orbit split WL$_n$, integrated intensity is proportional to the core states degeneracy: $r_{1,2} = I(L_1)/I(L_2) = 2$ and $r_{5,4} = I(M_5)/I(M_4) = 3/2$ (Fig. 3 and Table I). At the Cu L$_{2,3}$ edges: $r_{3,2}(\text{Cu:}3d^0 \text{CuO powder}) = 2.7$ for the Gaussian shaped WL (Table I, Fig. 2) is qualitatively explained by the presence of only one empty 3$d_{3/2}$ level at the top of the conduction band available for L$_3$ transitions but, only 4$d_{3/2}$ final states are available for L$_2$ transitions. The YBCO Cu:L$_{2,3}$ WL relative intensities (Table I) are similar to those for CuO, in agreement with a Cu:3$d^0$ oxidation state. At the Ba:L$_{2,3}$ edges the XAFS amplitudes, which measure the transition probability from the same core states to the empty continuum and obey the same orientation dependence as the WL, obtain for all samples a relative intensity proportional to core state degeneracy: $r_{3,2}(\text{Ba XAFS for YBCO}) = 2$ to within 4% accuracy (Table I). The significant deviations in YBCO WL: $r_{3,2}(\text{Ba in YBCO KKD powder}) < r_{3,2}(\text{Ba in YBCO single crystal}) < 2$ and $r_{5,4}(\text{Ba in YBCO film}) < 1.5$ (Table I) are explained by different transition probability due to final state 5$d$ and 4$f$ apparent occupation, respectively due to polarization. Since all orientations in $\varepsilon_{\text{X-rays}}$ are sampled for $r_{3,2}(\text{Ba in YBCO KKD powder})$, an apparent overpopulation of the 5$d_{3/2}$ states relative to the 5$d_{5/2}$ final states must be caused by polarons at $r_p$, and the same is true for the single crystal, though crystal field shifts and mixed valence effects are not resolved for a WL with HWHH$\sim 2.5$eV. Similarly $r_{5,4}(\text{Ba in YBCO film}) < 1.5$ indicates the effect of orientation, an apparent over population of 4$f_{1/2}$ relative to the 4$f_{5/2}$ levels and/or mixed valence.

The apparent difference in occupation of the spin orbit split final state bands in the non-magnetic YBCO$^{12b}$ may be qualitatively explained by the formation of $e_1e_2$ pairs with $j = j_1 + j_2 = 0$ in different layers where O states are involved in the highest occupied MO (Fig. 5)$^{13}$.

(iv) Line shape analysis gives additional evidence of charge polarization as follows: The difference spectrum, $\Delta(\text{Cu:}L_{2,3})$ leading sharp peak (HWHH$\sim 0.2$eV) at $E_0 + 0.5 \pm 0.1$ eV (first insert Fig. 2) suggests that in YBCO 50 nm film the ejected electron and X-ray hole form pairs, via a hydrogen like potential, in atomic units$^{10}$:

$$V(r) = -1/(K r) \text{ H when } r > r_p$$
$$= -1/(K r_p) \text{ H when } r < r_p$$

where $r_p$ is the radius of polarized charge and $K = 1/\varepsilon_{\infty} -1/\varepsilon_0$, when $\varepsilon_0$ and $\varepsilon_0$ are the material high frequency and static dielectric constants. In transition metal oxides $\varepsilon_{\infty} \sim 10$, and as high as 30 in La$_2$CuO$_4$ is meaningless in the region between atoms and $\varepsilon_{\infty} \lesssim 5$ to $8^{16}$. The hydrogen-like energy level eigenvalues$^{11}$ in (1): $E_n = -1/(2n^2K^2)$, $n = 1 \rightarrow \infty$ give rise to transitions at $h\nu$ where:

$$h\nu = E_n - E_1 = \frac{1}{2}(1-1/n^2)/K^2 \text{ H, } n \geq 2.$$  

An X-ray exciton head at:

$$h\nu = (0.5 \pm 0.1\text{eV})/(27.21\text{eV}/H) = 3/8K^2 \text{ H}$$

obtains $K = 4.2 \lesssim \varepsilon_{\infty}$ and $E_0 = -0.029\text{nH}$ predicts a sharp Rydberg series that ends sharply at $E_0 + 0.8$eV. The average separation $1<\nu> \sim K^2 0.053\text{nm/bohr} = 0.22\text{nm} > \text{CuO bond distance 0.195nm}$, when added to $r_p - 0.07$ to 0.08nm near Ba indicates an effect on their outer electron shell population is a possibility. This is similar to the formation of excitons in layer dichalcogenides observed in i.r. spectra$^{9,12a}$.

(v) Many electron interactions in bulk metals that are responsible for enhanced absorption to levels close to the Fermi energy$^{17}$ a few meV above $E_0$ are not be resolved here.

CONCLUSION

Spin-orbit split white lines in YBCO indicate an apparent overpopulation of the Cu:3$d_{3/2}$ final states relative to the 3$d_{5/2}$ as in CuO, and of the Ba:5$d_{5/2}$ final states relative to the 5$d_{3/2}$ as expected to 5$d^0$ occupation. The formation of X-ray excitons, observed at the Cu L$_{2,3}$ edges, and the orientation dependent changes in atomic XAFS at the Ba L$_2$ edge of a YBCO single crystal suggest that the formation of polarons is responsible for the apparent population of states near the Fermi level and these change near $T_c$.  

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TABLE I: Core $Z_{\text{eff}}$ and relative intensity of spin orbit WL, WL($E<E_0$) and XAFS$^{a,b}$

| ELEMENT (Z) | Changes in Occupied Shells | Changes in Occupied Shells | $Z_{2p,\text{eff}}$ | $Z_{3d,\text{eff}}$ | $|l(L_2)|/|l(L_2)|$ ± 0.1 | $|l(M_4)|/|l(M_4)|$ |
|-------------|-----------------------------|-----------------------------|-------------------|-------------------|-------------------|-------------------|
| CuO powder, TEY/l₁ | 0.726 | 3.1 | 3.1 |
| YBCO Film F/l₁: π/4 | 2.7 | 2.7 | 2.7 |
| YBCO Film TEY/l₁: π/2 | 3 | 2.8 | 2.8 |
| FINAL: Ba (56) | 53.6 | 13.82 | 13.82 |
| Sample Alignment: c$^a$€X$_{\text{en}}$ | 0.544 | 1.5 | 1.5 |

$^a$ The $\Delta E_{\text{experimental}}$ in atomic units, are set equal to the spin-orbit energy difference [ref. 8a] :
$\Delta E_{\text{SO}}(L_{2,3}) = [-Z^2_{\text{nd,eff}}/975 + Z^2_{\text{2p,eff}}/32]e^2H$, $\Delta E_{\text{SO}}(M_{4,5}) = [-Z^2_{\text{nd,eff}}/2150.4 + Z^2_{\text{3d,eff}}/405]e^2H$.  

$^b$ The finite sample thickness, $t$ absorption: $\text{abs}(E,t) = \int_0^t e^{-\eta(E)t}dt/\int_0^t\text{abs}(E)dt$, $\eta(E) = \Sigma_i\text{component}$ $\alpha_i(E)*\text{sample density}$, $\alpha_i = \text{element } i$ weight fraction, $\alpha_i(E) = \text{component } i$ cross section [ref. 7], obtains a ratio: $\text{abs}(E_{1/2,3})/\text{abs}(E_{1/2,3}) = 1.1$ at both the Cu L$_{2,3}$ and Ba M$_{4,5}$ edges in F, approaches 1 at the Ba L$_{2,3}$, and TEY surface probe, and is within the area measurements uncertainty limits. The XAFS amplitudes extrapolated to $E_0$, $\mu_0$ obtain intensity ratios equal to the freeBa$^{+}$ ion values to within ±4% error.

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