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 $E_0+0.5 \pm 0.1$ 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$^6$, 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. 2: YBCO film (e$_{film}$=e$_{rays}$ = $\pi$/4) compared to CuO powder, WL at the Cu L$_{2,3}$ edge: $E_0$(Cu:L$_3$) = 931.2 eV, $\Delta$=A$_{YBCO}$−A$_{CuO}$ (A normalized to L$_3$ amplitude maximum). Inserts show fit of sum G shape peaks (HWHH=0.45eV) to A$_{CuO}$ with less than 2% error and to $\Delta$ with less than 1% error if an exciton peak is included.
FIG. 3: WL at the Ba:M_{4,5} edges for YBCO film (c_{film} x_{cray}=π/4) and BaBr_2 powder. Weak shoulders in A BaBr_2 are due to (b) [ref.4, 5, 11]: ∆ or rp ~ N the appearance of a short wave oscillation, contributions to 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 X(k) cancel out in the XTDFAFS [ref.4, 5], and the appearance of a short wave oscillation, ∆k=4A^1 indicates N_p,T dependence at R_p = r_p obtained from the period 2r_p,∆k ~ 2π or r_p ~ π/∆k ~ 0.07 to 0.08 nm (when φ(k)~constant in the interval ∆k). (a) Increase in N_p across T_c when x_{cray} is in ab plane. (b) Decrease in N_p across T_c when x_{cray} is out of ab plane.

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 > 10^3 eV. The WL spectra are obtained by subtracting from A the empty continuum states, X-ray absorption fine structure, XAFS^{25,4} region (FIG. 1), except where the XAFS contribution from the previous edge is less than 2% at the Cu:L_2 and Ba M_4 edges in both YBCO and CuO (FIG. 2, 3).

FIG. 4: Change in atomic XAFS versus T, XTDFAFS for YBa_2Cu_3O_{7.8} single crystal at Ba L_2 edge through T_c. The XTDFAFS measure the changes in XAFS scattering amplitude [ref.4, 5, 11]: X(k)=∑ N_j sin(2k.R_j+φ(k))F(k.R_j/kR_j^2) 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 X(k) cancel out in the XTDFAFS [ref.4, 5], and the appearance of a short wave oscillation, ∆k~4A^1 indicates N_p,T dependence at R_p = r_p obtained from the period 2r_p,∆k ~ 2π or r_p ~ π/∆k ~ 0.07 to 0.08 nm (when φ(k)~constant in the interval ∆k). (a) Increase in N_p across T_c when x_{cray} is in ab plane. (b) Decrease in N_p across T_c when x_{cray} is out of ab plane.

(i) Evidence of charge polarization is obtained from atomic A-XAFS^{21} at distances less than an Å as follows: When the inter-atomic distances remain constant versus T, the changes in electron density, ρ_e near the heaviest element in YBCO, Ba are detected by the XAS temperature difference spectra, XTDFAFS^{4,5} amplitude versus k(bohr^(-1))=(2(E-E_0) H)^1/2 (FIG. 4). The observed oscillations identify a change in ρ_e near r_p ~ π/∆k ~ 0.07 to 0.08 nm from the Ba atom, across the transition to superconductivity, T_c that reverses sign when the polarized synchrotron electric field, x_{cray} is rotated out of the crystal ab plane. This indicates that polarons^{9,12} of radius r_p are involved.

(ii) The formation of polarons determines the symmetry and final states occupation and consequently the WL spectra relative intensity as follows: The XAS white lines (WL) observed at the Cu:L_{2,3} edges in CuO and cuprate superconductors show structure consisting of a main peak with gaussian, G shape (HWHH~0.45eV) plus weaker ones. The A_{CuO} additional structure indicates that the crystal field shifts in Cu:3d^9 may be described by G shape peaks with 3% of A_{CuO,max} and HWHH~0.45eV at E_p±1 to ±9eV, (FIG.3 insert) expected to be more complex than the V^1,3d^3 cubic crystal field splitting. The crystal orientation in x_{cray} determines the structure of spin-orbit WL pairs^{1,8}, but their separation,
\( \Delta E(\text{Cu}:L_{2,3}) \) is constant and dominated by the atomic core splitting\(^8\). The WL separation, \( \Delta E(\text{Cu}:L_{2,3}) = 19.7 \text{ eV} \) (FIG. 2) is the same as in other Cu compounds\(^8\) though the crystal field induced structure depends on the 3d\(^0\) filled Cu oxidation states\(^6\). Crystal field split peaks appear from \( E_0 + 0 \) to \( E_0 + 8 \text{ eV} \) in Cu metal, partially oxidized Cu film and Cu quantum dots respectively\(^6\), but the 10% absorbance present at \( E_0 + 7.2 \text{ eV} \) for both YBCO and CuO suggests that they have the same oxidation state Cu\(^{2-3d^2} \) in a distorted lattice. Their difference spectrum \( \Delta = \Delta \text{YBCO} - \Delta \text{CuO} \) vanishes to within less than 1% for \( E < E_0 \) at the Cu\( (L_{2,3}) \) edges but differs by as much as 20% \( W_{\text{Lmax}} \) for \( E > E_0 \) (insert FIG. 2) and may be described by a sharp (HWHH~0.2 eV) G shaped leading peak at \( E_0 + 0.5 \pm 0.1 \text{ eV} \) distinct from broader ones (HWHH~0.45 eV) at \( E_0 + 1 \pm 7 \text{ eV} \) (FIG. 2 insert). The first is too sharp to be assigned to a crystal field peak, the broader ones may be due to Cu\(^{2-3d^3}\) crystal field split 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)\(^9\). The Cu\(^{2-3d^4}\) 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\(^8\) while the Cu\(^{2-3d^4}\) splitting is reported to be twice as large\(^8\) 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~2.5 eV) for \( E < E_0 \) with \( \Delta E(\text{Ba}:L_{2,3}) = 376.2 \text{ eV} \) for YBCO and BaBr\(_2\) (FIG. 1, 3). The difference spectrum \( \Delta = \Delta \text{WLBa}-G \) for \( E > E_0 \) is orientation dependent with amplitudes 30% \( W_{\text{Lmax}} \) for \( E < E_0 \) in the ab plane that reduces to less than 10% of \( W_{\text{Lmax}} \) when \( E > E_0 \). The \( E(\text{Cu}:L_{2,3}) \) leading sharp peak (HWHH~0.2 eV) at \( E_0 + 0.5 \pm 0.1 \text{ eV} \) (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\(^8\):

\[
V(r) = -1/(K r^2) \text{ H when } r > r_p = -1/(K r_p)^2 \text{ H when } r < r_p
\]

where \( r_p \) is the radius of polarized charge and \( 1/K = 1/\varepsilon_{\infty} - 1/\varepsilon_0 \), when \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the material high frequency and static dielectric constants. In transition metal oxides \( \varepsilon_0 \sim 10 \), and as high as 30 in La\(_2\)CuO\(_4\) \(^6\) is meaningless in the region between atoms and \( \varepsilon \sim 5 \) to \( 8 \). The hydrogen-like energy level eigenvalues\(^8\) in (1): \( E_n = -1/(2n^2 \varepsilon_0^2) \), \( n = 1 \) to \( \infty \) give rise to transitions at \( h\nu \) where:

\[
h\nu = E_n - E_1 = \frac{1}{2}(1-1/n^2)/\varepsilon_0^2 \text{ H, } n \geq 2.
\]

An X-ray exciton head at:

\[
h\nu = (0.5 \pm 0.1 \text{ eV})/(27.21 \varepsilon_0^2 \text{ eV} \text{H}) = 3/8 K^2 \text{ H}
\]

obtains \( K = 4.2 \pm 0.5 \varepsilon_\infty - 0.029 n^2 \varepsilon_\infty \text{H} \) predicts a sharp Rydberg series that ends sharply at \( E_0 + 0.8 \text{ eV} \). The average separation \( 1/\nu = K \varepsilon_0 \text{K} = 0.053 \text{nm/bohr} = 0.22 \text{nm} > \text{CuO bond distance 0.195nm} \), when added to \( r_p - 0.07 \) to 0.08 nm 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\(_{3d_{5/2}}\) final states relative to the \( 3d^0 \) as in CuO, and of the Ba\(_{5d_{5/2}}\) final states relative to the \( 5d_{5/2} \) as expected to 5d\(^1\) 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 polaronic states is responsible for the apparent population of states near the Fermi level and these change near \( T_c \).
TABLE I: Core $Z_{eff}$ and relative intensity of spin orbit split WL, WL(E$<$E$_0$) and XAFSa,b

| WHITE LINE | Changes in Occupied Shells | Changes in Occupied Shells | $Z_{2p,eff}$ | $Z_{3d,eff}$ a | $|l(L_2^\alpha)|/|l(L_2)|$ ± 0.1 | $|l(M_2^\alpha)|/|l(M_2)|$ |
|------------------|----------------------------|----------------------------|--------------|-----------------|-------------------------------|----------------------------|
| Edge:            | L$_3$                      | L$_2$                      |              |                 |                               |                            |
| ELEMENT (Z)      |                            |                            |              |                 |                               |                            |
| CORE SHELL       | (2p$_{3/2}$)$^4$.           | (2p$_{1/2}$)$^2$.          |              |                 | 25.6                          |                            |
| FINAL:           | Cu (29)                    | Cu (29)                    |              |                 |                               |                            |
|                  | (2p$_{3/2}$)$^3$. (nd$_{3d}$)$^2$ n$_{\geq3}$ | (2p$_{1/2}$). (nd$_{3d}$)$^2$ n$_{\geq4}$ |              |                 |                               |                            |
| Sample Alignment:| c$^e$ɛ$_{Kx,corr}$         |                            |              |                 |                               |                            |
| CuO powder, TEYl$_0$ |                |                            | 0.726        |                 |                               |                            |
| YBCO Film F/I$_0$ | π/4                        |                            | 2.7          | 2.7             |                               |                            |
| YBCO Film TEY/I$_0$: | π/2                      |                            | 3            | 2.8             |                               |                            |
| FINAL:           | Ba (56)                    | Ba (56)                    |              | 53.6            |                               |                            |
|                  | (2p$_{3/2}$)$^3$. (nd$_{3d}$)$^2$ n$_{\geq5}$ | (2p$_{1/2}$). (nd$_{3d}$)$^2$ n$_{\geq5}$ |              |                 |                               |                            |
| Sample Alignment:| c$^e$ɛ$_{Kx,corr}$         |                            | 13.82        |                 |                               |                            |
| KKD YBCO powder, l/I$_T$ |                |                            | 1.7          | 2.7             |                               |                            |
| YBCO Single Crystal, l/I$_{H1}$: | 17π/36              |                            | 1.7          | 2.7             |                               |                            |
| Edge:            | M$_6$                      | M$_4$                      |              |                 |                               |                            |
| CORE SHELL       | (3d$_{3d}$)$^6$.           | (3d$_{3d}$)$^4$.           |              |                 |                               |                            |
| FINAL:           | Ba (56)                    | Ba (56)                    |              | 45.1            |                               |                            |
|                  | (3d$_{3d}$)$^5$. (of$_{5f}$)$^2$ n$_{\geq4}$ | (3d$_{3d}$)$^3$. (of$_{5f}$)$^2$ n$_{\geq4}$ |              |                 |                               |                            |
| Sample Alignment:| c$^e$ɛ$_{Kx,corr}$         |                            | 0.544        |                 |                               |                            |
| BaBr$_2$ powder, TEYl$_0$ |                |                            | 1.6          |                 |                               |                            |
| YBCO Film F/I$_0$: | π/4                        |                            | 1.1          |                 |                               |                            |

a The $\Delta E_{experimental}$ in atomic units, are set equal to the spin-orbit energy difference [ref. 8a]

b The finite sample thickness, $\alpha_{absorption}$: $abs(E,t) = \int_0^\infty e^{-\lambda(E,i)} dt = \frac{\eta(E)}{\alpha(E)} \int_0^\infty e^{-\lambda(E,i)} dt$. When $\eta(E) = \Sigma_{component} x_i \alpha(E) \times$sample density, $x_i$ = element $i$ weight fraction, $\alpha(E) = component$ i cross section [ref. 7], obtains a ratio: $abs(E_{1/2})/abs(E_{1/2}) = 1.1$ 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$^{2+}$ ion values to within ±4% error.

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REFERENCES

1. C.T. Lin, W. Zhou and Y. W. Liang, Physica C, 195 291 (1992)

2. M. A. Navacerrada, M. L. Lucia and F. Sánchez-Quesada, Europhys. Lett. 54, 387 (2001)

3. (a) M.A. Navacerrada and J.V. Acrivos, NanoTech 2003, 1, 751 (2003), (b) H.S. Sahibudeen, M.A. Navacerrada and J.V. Acrivos, NanoTech 3, in press (2005)

4. J.V. Acrivos, Solid State Sciences, 2, 807-820 (2000)

5. J.V. Acrivos et al., Microchemical Journal, 71, 117-131 (2002)

6. P. Nachimuthu et al., Chem. Mater. 15, 3939 (2003)

7. Center for X-Ray Optics, http://www.cxro.lbl.gov

8. (a) L.I. Sciff, “Quantum Mechanics”, McGraw Hill Book Co. Inc, 1949, p 280;(b) A. Abragam and B. Bleaney, “Electron Paramagnetic Resonance of Transition Ions”, Oxford (1970); (c) F.M.F. de Groot, J.C. Gugle, B.T. Thole and A.G. Sawartzyk, Phys. Rev B42, 5459 (1990)

9. (a) N.F. Mott, “Metal Insulator Transitions”, Taylor and Francis, ltd, 1974, 1990; (b) A.S. Alexandrov and N.F. Mott, “Polarons and Bipolarons”, World Scientific, Singapore (1995); (c) private communication (2005)

10. J.V. Acrivos and O. Stradella, International Journal of Quantum Chemistry, 46, 55(1993)

11. (a) A.L. Ankudinov and J.J. Rehr, J. Phys. IV France 7, 124-121 (1997); (b) A. Kodre, I. Arçon and R. Frahm, ibid, C2-195 (1997); (c) Y.A. Babanov, A.V. Ryazhkin and A.F. Sidorenko, ibid, C2-277 (1997)

12. (a) J.A. Wilson and A.D. Yoffe, Adv. In Physics 18, 193 (1969); (b) T.J. Smith et al., J. Magnetism Magn. Mater., 177, 543(1998)

13. Z.-X. Shen, W.E. Spicer et al., Science 267, 343 (1995)

14. (a) A. Bianconi et al, Phys. Rev. B38, 7196 (1988); (b) N. Nucker et al., Phys. Rev. B51, 8259 (1995)

15. J.V. Acrivos, Microchemical Journal, in press (2005)

16. G. Koster, T.H. Geballe and B. Moyzhes, Phys. Rev. B66, 085109 (2004)

17. M. Hentschel, D. Ullmo and H. Baranger, Phys. Rev. Lett. 93, 176807 (2004)

18. P. Glatzel, U. Bergmann et al., J. Am. Chem. Soc., 124, 9668 (2002)