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Exafs studies of phase transitions in high Tc cuprate superconductor

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DOI: <https://doi.org/10.31979/etd.z7u5-wvbq>
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**EXAFS STUDIES OF PHASE TRANSITIONS IN HIGH T_c CUPRATE
SUPERCONDUCTOR**

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Long Hoanghuan Nguyen

May 2000

UMI Number: 1399812

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ABSTRACT

EXTENDED X-RAY ABSORPTION FINE STRUCTURE (XAFS) STUDIES OF PHASE TRANSITION IN HIGH T_c CUPRATE SUPERCONDUCTOR.

By Long H. Nguyen

XAFS measurements are used to investigate the change in the local structure about the Ba and Nd atoms in the orthorhombic Superconductor $\text{Nd}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{7.8}$ near the superconducting transition temperature $T_c \approx 75\text{K}$. The Cu and Nd local structures are stable while the Ba and some O sites are disordered as the material undergoes the transition to superconductivity. It is shown that the Ba and O position are sensitive to the superconducting phase transition while the Cu and Nd are not.

ACKNOWLEDGEMENTS

I would like to thank Professor Juana V. Acrivos, for her guidance, support throughout the program, and extensive proof reading of this thesis. I also want to thank Professor Bradley Stone and Professor Robert Richardson for being part on my research committee.

Thanks are also due to NSF/DMR Research Grants at SJSU to the Acrivos Group and DOE for support at SSRL.

I would like to thank Acrivos Group for all their help.

A very special thanks to my mom and all my brothers and sisters for their love, support, and encouragement.

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I. INTRODUCTION

In 1986, J.G. Bednoz and K.A. Muller discovered the first high- T_c cuprate superconductor.¹ Soon afterwards, there was an explosion of theoretical and experimental work related to this field. Extended X-ray Absorption Fine Structure (XAFS) measurements have been used to study the system of High Temperature Superconductor $\text{Nd}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{7-\delta}$ (123), because it is a powerful tool for providing local structural information about an element.

1. STRUCTURE OF THE SUPERCONDUCTOR 123

The 123 are simple perovskite-like structures.² There are two $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ structures ($\delta = 0$ to 0.9): tetragonal and orthorhombic (Figure 1). The values for the orthorhombic 123 principal axes dimensions are (a, b, c) = (3.81, 3.88, 11.63 Å) with $\delta=0$ at 5K.³ These can change due to partial and/or full substitution of Y, Ba and/or Cu and also by the deficiency of oxygen ($\delta > 0.3$). The 123 structure consists of 7 sublayers.⁴ These planes are (Figure 2):

$\frac{1}{2}$ CuO (chain), BaO, CuO₂, Y, CuO₂, BaO, and $\frac{1}{2}$ CuO (chain).

All these sublayers are normal to the c-axis direction. The CuO₂ layer is not flat as shown in Figure 2. Each Cu(2) is surrounded by four nearest O(3) (1.94Å). In addition, Cu(2) also has another Cu(2) right below on the edge at a distance 2.45Å. The Cu(2)-O(3)-Cu(2) angle in 123 is about 167°. Oxygen atoms around Cu(1) do not form a perfect octahedral system, two Cu(1)-O(2) bond distances are 2.45Å and two to four Cu(1)-O(1) bond distances are at 1.8Å. In the Table 1, the bond distances between Y

and Ba to other atoms in the unit cell are calculated base on dimensions and the standard matrix as in Table 2.⁵

The CuO₂ layers have mobile charge carriers that are believed to be the core of superconductivity. Due to localized carriers, 123 has weak contact between the planes. Hence, it has extreme anisotropic properties – it is a poor superconductor in the c direction in both the normal and the superconducting state. Many theories of superconductivity are based on the experimental and theoretical evidence that the cuprate oxide planes play a major role in superconductivity and chains act as electron reservoirs which can be filled or emptied by the change of percentage of oxygen or by other types of doping.^{6,7}

1.1. TETRAGONAL 123

Tetragonal 123 transforms in the D_{4h}^{74} Space Group.⁸ The symmetry is D_{4h} about the Y atom. Y is at the center of the shell with eight fold coordination: eight Y-O(3) at (2.4Å) and eight Y-Cu(3) at (3.3Å). Ba has two shells of four fold coordination: four Ba-O(2) at (2.7Å) and four other Ba-O(3) at (2.8Å). The total oxygen content in tetragonal 123 may exceed seven per unit cell.

1.2. ORTHORHOMBIC 123

Orthorhombic 123 transforms in the D_{4h}^{14} space group.⁹ Dimension b is less than a due to empty space at O(1B) sites. The coordination in the orthorhombic is different

to the tetragonal 's. Y has two of four folds coordination shells: four of Y-O(3A), four of Y-O(3B), and eight fold coordinate to Cu(2).

The major difference between the orthorhombic and the tetragonal structures is the filling of oxygen at the position of O(1). In the ideal orthorhombic structure, O(1A) is fully occupied and the formula is $\text{YBa}_2\text{Cu}_3\text{O}_7$.

1.3. VARIATION OF Cu SUBSTITUTION

Cu has d orbital electrons. According to Fei et al,¹⁰ the controlling mechanism of superconductivity is associated with ionic radius primarily rather than with the charge of the doping element. There is a reverse relation between the oxygen content and cell's c dimension of the undoped material. This happens due to repulsion weakening between the Ba layers when the oxygen atoms fill up the chains. Increasing the coordination number for Cu(1) corresponds to expanding its ionic radius and lengthening the Cu(1)-O(1) bond. Increasing the charge of Cu(1) ions (smaller radius) causes decreasing of the cell dimensions and indirectly prevents the oxygen saturation of the lattice.

1.4. OXYGEN IN A SUPERCONDUCTOR

Oxygen stoichiometry significantly affects the physical properties of $\text{YBa}_2\text{O}_3\text{Cu}_{7-\delta}$. The fraction of the sample that was initially tetragonal ($\delta=0.1$) tends to remain tetragonal while the fraction that was initially orthorhombic ($\delta=0.9$) tends to

remain orthorhombic.¹¹ The oxygen atoms in the Cu-O chains are most likely to move out of the structure to become vacancies in the oxygen deficient samples of 123. Superconductivity not only depends on the deficiency of oxygen but also on the arrangement of the oxygen ions.¹² Also, Fei et al.,¹⁰ have proposed an electronic charge model that has ignored the magnetic moment interacting terms for the explanation of the high T_c mechanism. They found that the oxygen deficiency in the copper oxygen chain serves more in enhancing the formation of the antiferromagnetic phase in the oxygen deficient compound. This deficiency impedes the existence of superconductivity. As oxygen decreases, the overlap between Cu d-orbital increases; thus increasing the spin-spin coupling. The correct amount of spin-spin interactions determines the superconductivity.

1.5. SUBSTITUTION OF Y AND Ba

The substitution of other elements into the Y and Ba sites might either increase or decrease the charge balance of the material; in consequence, these substitutions will enhance or diminish the number of Cu-3d and O-2p holes.

1.6. ELECTRONIC STRUCTURE OF 123

The important structural features of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds arise from the fact that $(2 + \delta)$ oxygen atoms are missing from the perfect structure of perovskite $\text{YCuO}_3(\text{BaCuO}_3)_2$. The O vacancies in Cu plane (between the BaO planes) give rise to

the formation of Cu(1)O(1) chains. The double layers of Cu(2)-O(3A,B) planes in the superconductor yield a 2D structure.

The electronic structure is described by removing the linking oxygen atoms, without changing the interaction parameters. Starting from an empty chain, each additional oxygen atom introduces one anti-bonding level and two holes. If the level is above the Fermi energy, E_F , the antibonding level will absorb two holes and there is no doping in the cuprate layers. The whole count on the cuprate layer is modified only when the level lies below E_F .

The Cu configuration is $3d^9$ with one hole in the 3d shell and the O configuration is $2p^6$, a complete p shell. In the field of the crystal lattice the five Cu(3d) orbitals will lose their degeneracy, and the same will be true of the three O(2p) orbitals. In the independent electron tight-binding model, for instance, for a CuO_2 layer, there are 11 orbitals per unit cell and therefore, 11 bands are constructed from them. Because this conducting layer has only one hole, the Fermi energy intersects only the highest of these bands. And these highest lying orbitals have lobes that lie within a-b plane.

The 123 superconductors contain one formula unit per primitive cell. Both planes CuO_2 and chains CuO cross the E_F line in the Brillouin Zone (Figure 3).¹³ These four bands consist of two Cu2(3d)-O2(p)-O3(p) orbitals and two of Cu1(d)-O1(p)-O2(p) orbitals. Two strongly dispersed band C:

$$\text{Cu}(d_{x^2-y^2})(2) - \text{O}(p_x)(2) - \text{O}(p_y)(3)$$

have 2D character. The anti-bonding band A:

$$\text{Cu}(d_{z^2-y^2})(1) - \text{O}(p_y)(1) - \text{O}(p_z)(2)$$

is 1D dispersion from the linear chain cuprate. The π bonding band B is $\text{Cu}(d_{xy})(1) - \text{O}(p_z)(1) - \text{O}(p_y)(2)$.¹⁴

From the charge density calculation, the two dimensional cuprate planes and one dimensional cuprate chains have $dp\sigma$ bands. Y acts as an electron donor forming Y^{+3} ; it does not participate in the conduction electron density. The results of the calculation gives the average charge of Cu and O of 1.62 and -1.69 in the 1237 system. The main $\text{Cu}(2P_{3/2})$ peak and $\text{Cu}(2P_{1/2})$ are of d^{10} final state character where these electrons are transferred from ligands to Cu to fill the shell. There is also the appearance of the d^9 final-state character which exhibits multiple splitting due to the interaction between a $\text{Cu}(2p)$ core hole and an unpaired electron in the 3d shell.

The Y^{+3} and Ba^{+2} ions contribute to the stability of the high superconducting critical temperature and explain why it changes little. The isolated Y atoms can be replaced by strongly magnetic elements.

1.7. STRUCTURAL CHANGE IN A SUPERCONDUCTOR AT THE PHASE TRANSITION

The Acrivos group first discovered the increasing transparency of the superconductor only at near T_c (Figure 4).¹⁵ This indicates that the photoelectric effect is enhanced at the transition to superconductivity, suggesting that multiple scattering

phenomena are affected by the fluctuation present at the transition to superconductivity. As the next step, the positions of atoms in this structure were speculated to change at the critical temperature. These changes in bond length between the Y-O(3A, B) can be caused by two phenomena: the disorder of certain atoms and/or mixed valence states in an atom. For Pr doped in 123, there is distortion of Pr local structure, this distortion is due to interchanging between Pr^{3+} and Pr^{4+} but there is still a chance of the disorder of the other atoms.¹⁶ There is evidence of the short distance of Cu(2)-O(4) that can be explained as the impedance charge transfer between planes and the chains. From the data of Y and Pr K edges studied by Boyce et. al.¹⁷, there is a large amount of disorder and distortion in the CuO_2 planes. Also in the Cu K edges, there is a lengthening of the Cu(2)-O(4) bond. This helps explain the distortion in the CuO_2 planes. As another approach, the distortion may be due simply to a hybridization of the O(2p) and Pr(4f) electrons. The Pr valence is not 4+ but $\sim 3.33+$.

1.8. THESIS OBJECTIVE

X-ray Absorption Near Edge (XANES) and Extended X-ray Absorption Fine Structure (XAFS) Spectroscopies were used in this study to obtain the phase transition and the systematic disorder of atoms around Nd and Ba. Chapter I introduced systems of superconductor 123 and its related compounds, XAS techniques, and analysis processes. Experimental procedure including sample preparation and data collection are in Chapter II. The result and its derivation is discussed in chapter III and concluded in chapter IV

2. XAFS THEORY

XAFS measures the x-ray absorption coefficient μ as a function of photon energy E above the threshold of an absorption edge E_0 for atoms either in a molecule or embedded in a condensed phase. An X-ray photon with energy $E = h\nu$ above $E_0 = h\nu_0$ release a photoelectron from the absorber atom with energy:

$$\frac{1}{2} mv^2 = h\nu - h\nu_0 = E_K = \hbar^2 k^2 / 2m \quad (1)$$

This photoelectron expands as a spherical wave with a kinetic energy E_K and propagates with a wavelength $2\pi/k$, it has a probability for backscattering $F_j^2(k)$ from a neighboring atoms with phase shift $\phi_j(k)$. The propagating electron coherently returns to the original atom. This backscattered wave can interfere constructively or destructively with the original outgoing electron wave (Figure 5). As energy increases, the energy of the photoelectron increases and the wavelength decreases causing an alternating between destructive and constructing interference. This changing interference pattern modulates the transition matrix element of the photon absorption process. The transition of electrons into this continuum region of free electrons is modulated by an oscillatory structure, $\mu_0\chi(k)$ which has been called XAFS. The theoretical relation is:

$$\chi(k) = (\mu - \mu_0) / \mu =$$

$$\chi(k) = \sum_{i=1} \frac{n_s N_i}{k R_i^2} e^{-R_i/\lambda_i} e^{\sigma_i k^2} |f_i(k, \pi)| \sin |2kR_i + \alpha_i(k)|, \quad (2)$$

where μ_0 is the absorbance extrapolated to $k = 0$, n_s is the number of backscattering shells, N_i is number of atoms in i^{th} backscattering shell at a distance R_i , λ_i is effective photoelectron mean free path, σ_i is thermal and static disorder parameter, and $f_i(k, \pi)$ is backscattering amplitude function for the i^{th} shell. $\chi(k)$ depends on both the absorbing and scattering atoms and on the oxidation states of these atoms. The total phase difference between the leaving and returning wave is $2kR + \alpha_i(k)$ in which R is the distance between the absorber and the backscatterer. The Sum of phase shifts due to the scattering process of nearby atoms and the potential well around the absorbing atoms is then:

$$\alpha_j(k) = 2f(k) + \phi_j(k) - \pi, \quad (3)$$

$\phi(k, R_i)$ is the phase function (total phase shift experienced by photoelectron), it changes the origin with the frequency. It contains contributions from both the absorber and the backscatterer:

$$\phi_{ij}(k, R_i) = \phi_i(k, R_i) + \phi_j(k, R_i) - \lambda\pi$$

$$(4)$$

where $\lambda = 1$ for the K and L_I edges, and $\lambda = 2$ or 0 for the $L_{II,III}$ edges. The electrons at the central atom experience a phase shift twice, once going out and then coming back. But electrons at the neighboring atoms experience a phase shift only once when arriving and returning back to the absorber. The sinusoidal XAFS oscillation is caused by interference. $\sin(2kR_i + \alpha_i(k))$ with frequency $2R$ in k space. The larger R , the higher is the frequency of the oscillation. The XAFS amplitude is also reduced by $1/R^2$. Short Range Order (SRO) where the scattering of electrons from close neighbors, producing XAFS a few lattices spacing before attenuating gives the closest fit to the data. As the energy increases above the edge, there is a gradual decline in the absorption cross section μ_s . Simple theory predicts only this smooth decrease.

3. EXAFS DATA ANALYSIS

3.1. BACKGROUND REMOVAL

The interference function $\chi(k)$ in (2) obtains:

$$\chi(E) = (\mu(E) - \mu_0(E))/\mu_0(E), \quad (5)$$

the measurement obtains also the elemental absorption $\Delta\mu(E)$ from the experimental absorption (Figure 6). The pre-edge absorption curve can be fitted with a polynomial, a line, or a constant that is extrapolated beyond the edge (Figure 7). The elemental absorption still contains other background noises such as spectrometer base line, beam harmonics and elastic scattering. Spline fitting is a common method that uses least

square procedure to remove the low frequency background components from $\mu(E)$ without affecting the higher frequency XAFS oscillations. Spline fitting is the local fitting procedure where a polynomial function fits the changes. This method has problems when using higher order polynomials and many sections: it may remove parts of the XAFS oscillation and the signals. If low order or not enough sections are used, it will then distort the low distance peaks in Fourier transform.

3.2. NORMALIZATION AND μ_0 CORRECTION

Since the background $\mu_0(E)$ is affected by many other factors, it can not be used in the normalization procedure in a real experiment. One commonly used method to normalize $\Delta\mu(E)$ is to divide it with theoretical value calculated $\mu_{\text{victoreen}}$ or $\mu_0^{\text{th}}(E)$ (Figure 8):

$$\mu_{\text{victoreen}} = C\lambda^3 - D\lambda^4 \quad (6)$$

with C and D are true absorption coefficients and tabulated by McMaster. The XAFS equation then is

$$\chi = (\mu_{\text{data}} - \mu_{\text{spline}})/\mu_{\text{victoreen}} \quad (7)$$

3.3. CONVERSION OF E TO k (EXTRACTING XAFS)

The next step is to convert the photon energy E to photon electron wave vector k using equation (1), $k = 2\pi/\lambda_e = \{0.262(E - E_0)\}^{0.5}$ when E , k , and E_0 are in eV, $\text{\AA}^{-1}$, and the threshold energy is typically about 15eV above the calibration energy.

3.4. WEIGHTING SCHEME

In order to compensate for the attenuation of the XAFS amplitude at high k value $\chi(k)$ is multiplied by k^n to $\chi(k)$ (Figure 9 and 10). This will balance the amplitude. The k^3 multiplication gives more uniform EXAFS over the data range of k from 3 to $16\text{\AA}^{-1}$.

3.5. “DEGLITCHING” AND TRUNCATION

There are many discontinuities in data collecting such as glitches, spikes or steps in the data that will affect the background removal process. These discontinuities have to be removed before the background fit. Furthermore, data should be truncated at low and relatively high k . Shorter k range gives broader Fourier transform peaks and an effective resolution ΔR in bond lengths that decreases as $\Delta R = \pi/2k$ when the k range increases.

3.6. FOURIER TRANSFORM

The Fourier transform is used to convert the data from k-space to R-space. Upon integrating, the Fourier transform gives a peak shift from the true value of R (Figure 11). The bond length can be extracted by correcting this shift versus the system with known distances. The Fourier transform of $k^n \chi(k)$ in momentum (k) space gives a modified radial distribution function $\rho(R)$ in distance R-space:

$$\rho(R) = 1/(4\pi^{0.5}) \int_{k_{min}}^{k_{max}} k^n \chi(k) e^{i2kR} dk. \quad (8)$$

The Fourier transform equation including phase-correction is:

$$\rho(R') = 1/(4\pi^{0.5}) \int_{k_{min}}^{k_{max}} k^n \chi(k) e^{i2kR' + i\phi(k)} dk, \quad (9)$$

where $\phi(k)$ and Δ are appropriate XAFS phase function and the shift from true distance. Δ approximately equals to half the average phase shift slope for a given interaction. The parameters in the Fourier transform of a closed system must comply with the conservation rule:

$$N = N_s A R^2 / (A_s R_s^2), \quad (10)$$

where the subscript S stands for standard, N, A, and R are the number of atoms, Fourier transform peak magnitude, and distance respectively.

The Fourier transform is accurate for a system with well separated peaks and provides a simpler physical picture of local structure around the absorber; however it does have many other problems such as side lobe background peak that must be taken into account.

3.7. CURVE FITTING

This technique attempts to obtain the best fit to the function $k^n \chi(k)$ versus k with standard XAFS models. Amplitude and phase functions can be parameterized from a simple sum of Lorentzian curves:

$$F(k) = \sum_i \frac{A_i}{1 + B_i^2(k - C_i)^2}, \quad (11)$$

to a complicated ten-parameter form of Shulman:

$$F(k) = \frac{a_0 + a_1 k + \dots + a_5 k^5}{1 + a_6(k - a_{10}) + \dots + a_9(k - a_{10})^4}. \quad (12)$$

The parameterization of the amplitude and phase functions has advantages of reducing these functions and parameters. These parameters can be obtained by fitting the known model to a model and then transfer to the unknown system for structural determination (Figure 12). Using a simple Gaussian model, the parameters R , N , and σ^2 are obtained with an interatomic distance accuracy of ± 0.02 Å, a coordination number to ± 1 , and Debye-Waller factor (caused by thermal vibration and static disorder) in a typical range [0.0015, 0.008].

In addition to multidimensional parameter spaces, curve-fitting methods also include correlation among various parameters. The technique contains two sets of highly correlated variables: $\{F(k), \sigma, \lambda, N\}$ and $\{\phi(k), E_0, R\}$ in which N correlates with σ^2 and R correlates with E_0 . The resolution by XAFS is limited by the Uncertainty Principle:

$$\Delta R \cdot \Delta k \geq \pi/2, \quad (13)$$

where ΔR is the spread of distance and Δk is the data range.

3.8. THEORY OF MULTIPLE SCATTERING

The standard theory of x-ray absorption fine structure used for structural analysis is based upon a multiple-scattering formalism. Single scattering is mostly used to measure the nearest-neighbor distances, while higher-order multiple scattering contributions are important in quantitative calculation of XAFS. Multiple scattering

terms are required for determining the second and third nearest neighbor distances and bond angles.

The standard theory of XAFS is based upon the assumption of a spherical muffin-tin scattering potential: where the potential seen by the photoelectron is composed of non-overlapping, spherically symmetric potentials around each atom and is flat between the different atomic-like potentials.

The multiple scattering (MS) problem is based on perturbation theory in the direction of the scattering potential. It is called a “path” approach.¹⁸ The perturbation expansion is expressed in terms of a hypothetical path in which an electron scatters and propagates atom to atom. Also in the high-energy region, the multiple scattering corrections are weaker and the simplifying plane-wave becomes more accurate. The path formalism depends on the lifetime effect that allows the possibility to truncate the multiple scattering expansion such that only path lengths less than a few mean free paths are retained.

The photoelectron wave is scattered from more than one scattering atom in multiple scattering. Photoelectron waves returning to the central atom from MS paths are thought to mostly cancel each other or undergo significant amplitude reductions because of inelastic scattering effects. However, in some compounds, forward scattering paths among linear or near linear atoms have been shown to increase amplitude relative to the single scattering predictions.

II. XAS EXPERIMENT

1. SAMPLE PREPARATION

The Beer-Lambert Absorbance Law,

$$\ln(I_0/I) = \mu x \quad (14)$$

is written in terms of the mass absorption coefficient or cross section, α , in units of area/weight equal to, the density of the sample, d , in units of weight/volume, times the sample thickness, x (Figure 13). The absorbance is:

$$A = \ln(I_0/I_1)/\ln(10) = \langle \alpha d x / 2.303 \rangle \quad (15)$$

The optimum value for relation (15) is 0.9. This gives the mass absorption coefficient α as function of the energy for the different atoms in units of cm^2/g . The linear absorption coefficient, μ , is equal to this constant, α , times the density, d , of the absorber. Relationship (15) holds for each individual component and is the sum of all individual atoms. Then for a given density d_i of component i in solution or in a solid of thickness x_i :

$$x_i \mu_i = \alpha_i d_i x_i \quad (16)$$

The average thickness times the linear absorption coefficient for a solution containing many components is then:

$$x \mu = \sum u_i x_i = \sum \alpha_i d_i x_i \quad (17)$$

Near the absorber edge energy of component 1, this contributes most the absorption of the system. The only changes that occur are in its linear absorption coefficient below the edge:

$$\mu_{l-} = \alpha_{l-} d_l, \quad (18)$$

and the value above the edge:

$$\mu_{l+} = \alpha_{l+} d_l \quad (19)$$

Then $x \mu$ changes as:

$$x \Delta\mu = x_l \Delta\mu_l = \Delta\alpha_l d_l x_l, \quad (20)$$

where the change in the mass absorption coefficient:

$$\Delta\alpha_l = \alpha_{l+} - \alpha_{l-} \quad (21)$$

is obtained from the CRC Tables ¹⁹ and $d_l x_l$ must be determined for maximum signal to noise ratio. From (15) it follows that:

$$A = x \mu / \ln 10 \quad (22)$$

where A should change at the edge by 90% for maximum signal to noise ratio, i.e.,

$$\Delta A / (x \mu) = x_l \Delta\mu_l / (\mu \ln 10) \quad (23)$$

$$= (\text{weight})_l \Delta\alpha_l / (2.303 (\text{area})_l x \mu) = 0.9.$$

The calculation of the sample thickness is done to minimize the absorbance of the inert components at the interested edge. The inert component used is BN with a density of 2.25 g/cm^3 . The calculation of the optimum sample concentration for the BaL_{II} edge is used as an example for a sample thickness of 0.2 cm with information on α_l of B, N, and Ba in Table 3:

$$\begin{aligned} A = x \mu &= \sum u_i x_i = \sum \alpha_i d_i x_i \\ &= ((10.8 \cdot 7.23 + 14.45 \cdot 14) / (10.8 + 14)) \cdot 2.25 \cdot 0.2 / 2.3 \\ &= 2.21 \end{aligned}$$

At the BaL_{II} edge, Ba will contribute (90%) to the absorbance. The inert material is part of the background absorption. If the total absorbance is 1, relation (20) is used to calculate the weight of the sample that should be added to the sample, i. e.,

$$x \Delta\mu = x_l \Delta\mu_l = \Delta\alpha_l d_l x_l$$

or
$$d_l x_l = 1/(660-587) = 0.0137 \text{ g/cm}^2$$

For a sample area of $0.4 \times 1.8 \text{ cm}^2$, the amount of 123 should be

$$W = 0.0137 \times 1.8 \times 0.4 = 0.00986 \text{ g}$$

diluted with $(0.2 \times 0.4 \times 1.8) \times 2.25 = 0.36 \text{ g}$ of BN

2. DATA COLLECTION AT SSRL.

The intense synchrotron x-ray source at SSRL is emitted when charged particles move near the speed of light in magnetized curved path of the SPEAR storage ring at the Stanford Linear Acceleration Center (SLAC) (Figure 14).²⁰ Synchrotron Radiation (SR) is used as a broad band, tunable x-ray source. The advantages of SR x-rays are high intensity, tunability over a wide range of energy, and precisely pulsed time structure. (10^{-9} s pulse at 10^{-6} s)

Continuous energy x-rays are produced using a double silicon-crystal diffraction monochromator (Figure 15). Two parallel crystals diffract the beam according to Bragg's law:

$$n\lambda_{hkl} = 2d_{hkl}\sin\theta_B \quad (24)$$

where λ_{hkl} , n , and d_{hkl} are wavelengths of the diffracted x-rays, harmonic order, and lattice spacing for that plane at a Bragg angle θ_B from the beam direction. Under PDP-11 computer system control, the entire monochromator assembly is rotated so that θ_B changes at a constant rate of motor step per unit time; thus, the x-ray wavelength is swept across the energy range of interest.

Solid state ion chambers are used at SSRL to measure the high intensity of the x-rays. Three ion chambers (Figure 16) are used to measure the intensity of the incident x-ray beams I_0 after absorption I_1 and to measure x-ray absorption reference edges for wavelength calibration. This consists of an ionization chamber mounted upstream of the input beam collimator with associated current-sensing electronics to measure the incident beam flux. Usually the front and back chambers are 6" and 12" long. At the energy range less than 15keV, helium is used while with the range above 15keV nitrogen is used instead.

3. COMPUTER INTERFACE

A MicroVAX II computer running the latest version of the CADS-4 software from Engraf-Nonius Corporation controls the CAD-4 system. The computer is tied into the SSRL ethernet and is equipped with a TK50 tape drive.

The energy of the x-ray beam is tuned by a 2-crystal monochromator. Detuning the monochromator crystals eliminates higher energy harmonics in the beam. For an energy range less than 17 keV, a Si crystal cut on 111 plane is used. There is a temperature control system available to cool the Si crystal. Liquid He is used to cool

the sample down to as low as 5 K in an Oxford Cryostat. Program package XAS supports sample crystal alignment calibration of x-ray energy, crystallographic data collection, and processing of collected data.

4. ANALYSIS PROCEDURE

FEFF 5¹⁸ is used for the data analysis. At first the model of fitting must be created from the XRF information. Distance and coordination of an atom from the center atom (absorber atom) are generated from this model. For Nd atom in Nd_{1.1}Ba_{1.9}Cu₃O_{7-δ}, the model includes three single scattering shells and two multiple scattering shells (Figure 17 and Table 4). The first three single scattering shells are relatively closed to the center atom. Multiple scattering shells are distant from center absorber atom. The bonds to atoms in these distant shells must colinear with the absorber, first scatterer, and itself in Table 3. In the same manner, the model for Ba fitting includes 6 single scattering shells and three multiple scattering shells (Figure 18 and Table 5). Utilizing the FEFF 5 and EXAFSPAK²¹ to do the analysis, some constraints must be used to fit the model:

E_0 must be kept the same for all paths and is floated while distances and σ^2 are kept the same.

E_0 and σ^2 are then floated and linked in all paths, while distances are floated.

The results of the lowest temperature run is fitted first; then these results are used to fit the system at different temperatures.

The results are partially shown in table 6 and 7.

III. RESULTS & DISCUSSIONS

The XAFS analysis was done both on the X-Ray Absorption Near Edge (XANES) and XAFS regions.

XANES provides information on the oxidation state of the absorber. The edge position increases linearly with the valence of a number of metals.²² The symmetry allowed transitions from Ba L core states $P_{3/2}$ and $P_{1/2}$ to s or d-symmetry state obtain the XANES white peak. The ratio of $A/\Delta A$ (μ) measures the d character of the excited states for L_{II} and L_{III} edges.²³ The analysis was done on $Nd_{1-x}Ba_{1.9}Cu_3O_{7-x}$ superconductors. A and μ are plotted versus the temperature and energy (Figure 19). Also the threshold energy E_0 is measured but does not give quite reliable results.

X-Ray Temperature Difference Spectra (XTDAFS) were obtained:

$$\begin{aligned} XTDAFS \equiv DX &= k^n [X(T) - X(T_0)] = \\ &= \sum_j 2 * \{ F(k_j) / r_j^2 \exp(-\sigma^2 k_j^2 - 2r_j / \lambda_j) * \\ &\quad \cos[2k_j r_j + (\phi_{j,T} + \phi_{j,T_0})/2] * \sin[(\phi_{j,T} - \phi_{j,T_0})/2] \} \end{aligned} \quad (24)$$

The XTDAFS (Figure 20) show that there is no change or very little change vs T in the XANES region. From the analysis of the data a number of results are observed:

The samples become transparent near T_c in the XAFS region of Ba $L_{II,III}$ edges. The fluctuation of these two edges (Figure 21) maybe due to fluctuation of electron density.

XTDAFS of Nd L_{III} edge does not fluctuate (Figure 22).

Multiple scattering fits were first done on the structure of Nd-Substituted 123. The analysis was done on Ba L_{III} and Nd L_{III} edges.

For Nd L_{III} analysis, distances from the absorbers were graphed against temperature. The distance between Nd and O(3A, 3B) and Cu(2) atoms do not change as the superconductor goes through phase transition as in Figure 23 and 24. Assumption can be made that either Nd with Cu(2) and O (3A,B) in cuprate plane do not fluctuate or they all fluctuate at the same time. The second assumption seems to be more unreal.

In this analysis, the first two shells include 4 O(3A) and 4 O(3B), the next shell includes 8 Cu(2). These three shells are important in the fitting. The Fourier transform of the data obtains peaks at the 4 and 5 Å. This shows that there are penetrations of the scattering electrons through these nearest neighbor shells. There must be backscattering atoms at these distance intervals. The next shell is Ba(2) that is in the same unit cell of the primary unit cell and is not important in the fitting. The rest are Nd(100, -100) and Nd(010, 0-10) that are 1 cell unit distance from the Nd of the primary unit cell, Ba(100, -100) and Ba(010, 0-10) that are also 1 cell unit distance from Nd of the primary unit cell, and Y(110, 1-10, -110, -1-10) that is diagonal in unit distance from Y of the primary unit cell.

In the analysis of Ba L_{III} , an increase in the Ba-O(1A) and Ba-O(3A) distances and an unchange in the Ba-O(3B) bond distance implies Ba moves along b direction parallel to cuprate chain (Figure 25, 26, 27 and 28).

The motion of the Ba atoms near T_c is mapped in Figure 29.

Nd does not move relatively to Ba.

Near T_c , the XTDAFS change the multiple scattering due to fluctuations near T_c that would give rise to slow changes in the first two terms in relation (24), changes in

the potential sensed by the backscattered electron affect the phase shift which may then undergo the fluctuations of wave length of the order ϵ .

IV. CONCLUSIONS

The increased transparency near T_c in the XAFS region suggests a decrease in the electron density in the path of x-rays. The correlation of the observed increased transparency with the increased bond distance should depend on the electron density.

There is no fluctuation of XTDAFS because Nd is held tightly between two CuO layers (Figure 24).

Bond distances r are related to the overlap transfer integral $t(\beta)$ which gives rise to the conductivity:

$$t(\beta) = t_0 \exp(-r/a_0);$$

t decreases with bond density giving rise to a greater bond distance r .

Change in the electron density allows the Ba atom to move in and out of the equilibrium.

The Ba motion along the b direction a distance $0.1\text{\AA}$ may be caused by an increase of the electron density along chains near T_c .

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Figure 1. Tetragonal Structure and Orthorhombic Structure of YBa₂Cu₃O_{7.8}.²⁴

Orthorhombic structure has no Oxygen at O(1B) positions, causing a different a and b dimensions.

Figure 2. The structure contains seven sub-layers that include 2 CuO chains, 2 BaO planes, 2 Cu₂O planes, and Y plane.

Figure 3. Energy bands of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ plotted along several directions in the Brillouin Zone.¹³ The Fermi energy is 0.0. Two strongly dispersed bands C $\text{Cu}(d_{x^2-y^2})(2) - \text{O}(p_x)(2) - \text{O}(p_y)(3)$ have 2D character. The anti-bonding band A $\text{Cu}(d_{z^2-y^2})(1) - \text{O}(p_x)(1) - \text{O}(p_z)(2)$ is 1D dispersion from the linear chain cuprate. The π bonding band B is $\text{Cu}(d_{xy})(1) - \text{O}(p_z)(1) - \text{O}(p_y)(2)$.

Figure 4. Increasing transparency of Superconductor near T_c . Near critical temperature, the absorbance decreases in XAFS region.

Figure 5. Backscattering of photoelectron between absorber and backscatterer.

Outgoing wave and backscattering wave can either constructively or destructively interfere causing a modulation of absorbance in XAFS region.

Figure 6. X-ray absorption spectrum ($\mu x = \text{abs}$) vs E for Ba L_{II} edge of $\text{Nd}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_7$. L_{II} edge of Ba corresponds to the ejection of 2p electron by absorption of a photon with $E \geq E_0$. E_0 is the threshold energy.

Figure 7. Subtracted pre-edge and truncated of the BaL_{II} spectra. The pre-edge region for BaL_{II} (5500-5480) is fitted with a polynomial that can be extrapolated beyond the edge. The pre-edge fit is then subtracted from the absorption data (raw data).

XAFS, SPLINE REMOVAL USING VICTOREEN POLYNOMIAL, 04/96

Figure 8. Spline removal of the data to convert the subtracted pre-edge data.

Normalized $\Delta\mu$ is a difference between absorption data and Spline function

(background function). XAFS $\chi(E)$ is redefined as the result of division of normalized

$\Delta\mu_e$ over μ_{Spline}

Figure 9. $\chi(E)$ is converted to $\chi(k)$ with k is photoelectron wave vector $k = 2\pi/\lambda_e$.

Figure 10. $\chi(k)$ is multiplied with kn to compensate the attenuation of the data.

$\chi(k) \cdot k^3$ is called weighted EXAFS spectra.

Figure 11. Fourier Transformation of weighted EXAFS in k space into radial distribution space is plotted thin curve. Thick curve is the Fourier transformation of the model.

Figure 12. $\chi(k)$ Fitting curve from back transform. The thin spectrum is the weight EXAFS spectrum. The thick curve fits the data with the model by the curve fitting technique.

Figure 13. Intensity of beam line and sample with thickness x . The absorbance is defined as $\mu x = \ln (I_0/I_1)$.

Figure 14. SPEAR storage ring at Stanford Linear Acceleration Center (SLAC). X-ray is emitted by electrons moving at high speed in a magnetic curve path (storage ring).

Figure 15. Double Silicon-Crystal

Figure 16. Transmission absorption setup for the experiment

Figure 17. Nd fitting model includes 3 single scattering and 2 multiple scattering paths.

Figure 18. Fitting model for Ba atom includes 8 single scattering and 3 multiple scattering paths.

Figure 19. A and Mu are plotted versus Temperature. Mu measures the excited states for L_{II} edge of Ba. Two excited states are around 90K and 50K.

Figure 20. X-ray Temperature Difference Absorption Fine Structure of Ba L_{II} edge versus temperature. The graph shows significant fluctuation of absorption in XAFS region near critical temperature

EXAFS 23,24_DBaL2 Jun95, EXAFS vs T

Figure 21. X-ray Absorption Fine Structure of BaL_{II} edge versus temperature.

Figure 22. X-ray Absorption Fine Structure of NdL_{III} versus temperature. The graph shows no significant change of absorption in the XAFS region as temperature going through critical temperatures.

Figure 23. Distance from Nd to O(3A,3B) as temperature decreasing.

Figure 24. Distance from Nd to Cu(2) and Ba as Temperature decreasing.

Figure 25. Distance From Ba to O(2) as temperature decreasing. Ba-O(2) bonds change at or near critical temperature. The change is significant and well above analysis error.

Figure 26. Distance from Ba to O(1A,3A) as Temperature Decreasing. Same observation as Figure 25.

Figure 27. Distance from Ba to O(3B) as temperature decreasing.

Figure 28. Distance from Ba to Cu(1, 2) as temperature decreasing.

Figure 27. Motion of Ba along the b direction.

Layer	Bond Y to Atoms	R (Å)	N	Bond Ba to Atoms	R (Å)	N
$\frac{1}{2}$ CuO (chain)	Y-O1A	6.1196	2	Ba-O1A	2.8296	2
	Y-Cu1	6.4199	4	Ba-Cu1	3.4309	4
BaO (plane)	Y-Ba	3.7240	1	Ba-Ba	0.0000	
	Y-O2	4.7746	4	Ba-O2	2.7274	4
CuO ₂ (plane)	Y-Cu2	3.2308	4	Ba-Cu2	3.3647	4
	Y-O3A	2.4280	2	Ba-O3A	2.9129	2
Y	Y-O3B	2.4008	2	Ba-O3B	3.0227	2
	Y-Y	0.0000		Ba-Y	3.7240	1
CuO ₂ (plane)	Y-O3B	2.4008	2	Ba-O3B	6.4510	2
	Y-O3A	2.4280	2	Ba-O3A	6.810	2
BaO (plane)	Y-Cu2	3.2308	4	Ba-Cu2	4.9890	4
	Y-O2	4.7746	4	Ba-O2	3.4309	4
$\frac{1}{2}$ CuO (chain)	Y-Ba	3.7240	1	Ba-Ba	7.4038	1
	Y-Cu1	6.4199	4	Ba-Cu1	9.8981	4
	Y-O1A	6.1196	2	Ba-O1A	9.7061	2

Table 1. Distance between Y and Ba to other atoms in the cell

Tetragonal $P4/mmm$ (D_{4h}^7)
 $A = b \cong 3.9 \text{ \AA}$ $c \cong 11.8 \text{ \AA}$ $Z = 1$

Atoms	Site	Symmetry	x	y	z
Y	1d	4/mmm	1/2	1/2	1/2
Ba	2h	4mm	1/2	1/2	0.19
Cu1	1a	4/mmm	0	0	0
Cu2	2g	4mm	0	0	0.36
O1	2f	mmm	0	1/2	0
O2	2g	4mm	0	0	0.15
O3	2i	mm	0	1/2	0.38

Orthorhombic $Pmmm$ (D_{4h}^1)
 $a = b \cong 3.9 \text{ \AA}$ $c \cong 11.8 \text{ \AA}$ $Z = 1$

Atoms	Site	Symmetry	x	y	z
Y	1h	mmm	1/2	1/2	1/2
Ba	2t	mm	1/2	1/2	0.19
Cu1	1a	mmm	0	0	0
Cu2	2q	mm	0	0	0.36
O1A	1b	mmm	1/2	0	0
O1B	1e	mmm	0	1/2	0
O2	2q	mm	0	0	0.16
O3A	2r	mm	0	1/2	0.38
O3B	2s	mm	1/2	0	0.38

Table 2. Standard matrices for Orthorhombic and Tetragonal systems.⁵

	B	N	Ba
X-ray Cross Section	5.41K eV 7.23	5.41 K eV 14.5	5.41 K eV 587 5.9 K eV 660
Atomic weight	10.8	14	137.33

Table 3. X-ray Cross Section and Atomic Weight of Atoms for sample Calculation

Paths	Geometry	R (Å)	N	Bond Type
1	Nd→O3A→Nd	2.4460	4	Single
2	Nd→O3B→Nd	2.4279	4	Single
3	Nd→Cu2→Nd	3.2612	8	Single
4	Nd→Ba→Nd	3.7340	2	Single
5	Nd→Nd*→Nd	3.8613	2	Single
6	Nd→Nd**→Nd	3.9067	2	Single
7	Nd→O3A→Ba*→O3A→Nd	5.3714	4	Triple
8	Nd→O3B→Ba**→O3B→Nd	5.404	4	Triple

Table 4. Model for Nd fitting. (Ba* and Nd* are in cells 100 and -100, Ba** and Nd** are in cell 010 and 0-10)

Path #	Geometry	R (Å)	N	Bond Type
1	Ba→O2→Ba	2.7556	4	Single
2	Ba→O1A→Ba	2.8759	2	Single
3	Ba→O3A→Ba	2.9884	2	Single
4	Ba→O3B→Ba	2.9737	2	Single
5	Ba→Cu(2)→Ba	3.3831	4	Single
6	Ba→Cu(1)→Ba	3.4766	4	Single
7	Ba→Ba*→Ba	3.8613	2	Single
8	Ba→Ba**→Ba	3.9067	2	Single
9	Ba→O3A→Nd*→O3A→Ba	5.4042	2	Triple
10	Ba→O3B→Nd**→O3B→Ba	5.3714	2	Triple
11	Ba→O→Ba***→O→Ba	5.4929	4	Triple

Table 5. Model for fitting of Ba (Ba* and Nd* are in cells 100, -100, and Ba** and Nd** are in cells 010, 0-10, Ba*** belongs to cells 110, -110, 1-10, -1-10)

Path	Geometry	N	R (Å)	R _{refRD} (Å)	σ^2 (Å ²)
1	Nd→O3A→Nd	4	2.4460	2.4330	-0.004
2	Nd→O3B→Nd	4	2.4279	2.2956	0.007
3	Nd→Cu2→Nd	8	3.2612	3.258	-0.003
4	Nd→Ba→Nd	2	3.7340	3.827	-0.011
5	Nd→Nd*→Nd	2	3.8613	3.946	-0.006
6	Nd→Nd**→Nd	2	3.9067	4.012	-0.011
7	Nd→O3A→Ba*→O3A→Nd	4	5.3714	5.3173	-0.011
8	Nd→O3B→Ba**→O3B→Nd	4	5.404	5.4646	-0.012
9					

Table 6. Fitting Data for the lowest temp. file for Nd L_{III} edge . (Ba* and Nd* are in cells 100 and -100, Ba** and Nd** are in cell 010 and 0-10)

Path	Geometry	N	R (Å)	R _{xafs} (Å)	σ^2 (Å ²)
1	Ba→O2→Ba	4	2.7556	2.760	0.010
2	Ba→O1A→Ba	2	2.8759	2.970	0.012
3	Ba→O3A→Ba	2	2.9884	2.929	0.012
4	Ba→O3B→Ba	2	2.9737	3.111	0.035
5	Ba→Cu(2)→Ba	4	3.3831	3.345	0.012
6	Ba→Cu(1)→Ba	4	3.4766	3.511	0.008
7	Ba→Ba*→Ba	2	3.8613	3.828	0.019
8	Ba→Ba**→Ba	2	3.9067	3.888	0.011
9	Ba→O3A→Nd*→O3A→Ba	2	5.4042	5.392	0.007
10	Ba→O3B→Nd**→O3B→Ba	2	5.3714	4.957	0.010
11	Ba→O→Ba***→O→Ba	4	5.4929	5.173	0.009

Table 7. Fitting data for the lowest temperature of BaL_{III} edge (Ba* and Nd* are in cells 100, -100, and Ba** and Nd** are in cells 010, 0-10, Ba*** belongs to cells 110, -110, 1-10, -1-10)