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UNIVERSITY OF CALIFORNIA, SAN DIEGO

**X-ray diffuse scattering studies of the local
structural inhomogeneities in high temperature
superconductors**

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in

Physics

by

Xuerong Liu

Committee in charge:

Sunil K. Sinha, Chair
Dimitri N. Basov
Zahirul Islam
Sungho Jin
M. Brian Maple
Edward T. Yu

2009

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The dissertation of Xuerong Liu is approved, and it is acceptable in quality and form for publication on microfilm.

Chair

University of California, San Diego

2009

To my wife Jing

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Acknowledgments

First of all, I would like to thank my thesis advisor, Sunil Sinha for having taught me so much about many different aspects of physics. His provoking guidance, constant support and encouragement have escorted me through many difficulties I have encountered in this work on the high temperature superconductors, one of the most fascinating and challenging classes of materials in condensed matter field.

I owe a great and special thank-you to Zahirul Islam at the Advanced Photon Source at Argonne National Laboratory, who has been my mentor on the X-ray scattering techniques. Over the past several years, Zahirul Islam has guided me through every experimental details and contributed so much to my knowledge and experience. His efforts and knowledge are the key ingredients of this research. Also, his passion and serious attitude on science and experiments have influenced me tremendously and will certainly benefit my future.

I am grateful to Simon Moss for many helpful discussions and contributions. I thank Robert McQueeney for helping with rigorous thermal diffuse scattering calculations. I would also thank Ulrich Welp and Shuichi Wakimoto for providing the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples used in the experiments. I thank David Hinks, Helmut Claus, Jennifer Zheng, John Mitchell and M. Brian Maple for allowing me to use their instruments to process and characterize our samples. I benefited greatly from interactions with my

former officemate Elizabeth Blackburn.

Last, but not the least, I owe so much to my family, especially my wife Jing. Thanks for their love, support and understanding. Thanks for being there for me, always.

This research was funded by DOE Grant No. DE-FG02-03ER46084. Most of the experiments were conducted on the X-Ray Operation and Research 4-ID-D beam line at the advanced Photon Source. I would like to acknowledge the help and support from Jonathan C. Lang, group leader of the 4-ID-D beamline. Use of APS was supported by the DOE contract No. DE-AC0206CH11357.

Chapter 4 contains materials in

- X. Liu, E. Blackburn, Z. Islam, S. K. Sinha, R. J. McQueeney and S. Wakimoto, “Local lattice distortion in underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor”, in preparation(2009)

Chapter 5 contains materials in

- Z. Islam, X. Liu, S. K. Sinha, J. C. Lang, S. C. Moss, D. Haskel, G. Srajer, P. Wochner, D. R. Lee, D. R. Haeffner and U. Welp, “Four-Unit-Cell Superstructure in the Optimally Doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ Superconductor”, Phys. Rev. Lett. 93, 157008 (2004). Copyright(2004) by the American Physical Society.
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Curriculum Vitæ

Education

- 2009 Doctor of Philosophy in Physics
University of California at San Diego, La Jolla, CA
- 2001 Bachelor of Science in Physics
University of Science and Technology of China, Hefei, Anhui, P. R.
China.

Research Experience

- 2002–2008 Research Assistant, Department of Physics
University of California at San Diego, California, USA
Advisor: Sunil K. Sinha, Department of Physics, University of California at San Diego

Teaching Experience

- 2001-2002 Teaching Assistant, Department of Physics
University of California at San Diego, California, USA

Publications

X. Liu, E. Blackburn, Z. Islam, S. K. Sinha, R. J. McQueeney and S. Wakimoto, “Local lattice distortion in underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor”, in preparation.

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ABSTRACT OF THE DISSERTATION

X-ray diffuse scattering studies of the local structural inhomogeneities in high temperature superconductors

by

Xuerong Liu

Doctor of Philosophy in Physics

University of California, San Diego, 2009

Sunil K. Sinha, Chair

The high temperature superconductivity in cuprates is realized by off-stoichiometric doping. In addition to contributing carriers to the CuO_2 planes, the dopants inherently introduce local disorder into the systems. Using the X-ray diffuse scattering technique, we studied the dopant-induced local structural distortions in two cuprate compounds: $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$.

On $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$, strong anisotropic diffuse scattering pattern on top of the diffuse scattering due to thermal vibrations was observed. Our quantitative analysis shows that the observed anisotropic X-ray diffuse scattering intensities can be well described by the Huang Diffuse Scattering(HDS) theory with the single defect approximation, which indicates the Sr dopants are randomly distributed in the crystal. Based on the fitted parameters, the Sr-dopant induced elastic lattice distortion pattern was reconstructed. The

big amplitude of the elastic lattice distortion near the Sr dopants suggests that Sr-dopant induced local structural modulation might be the origin of the electronic inhomogeneities observed with scanning tunneling microscopy experiments.

The oxygen vacancies in $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ behave in a different way. Our X-ray diffuse scattering measurements reveal that majority of the oxygen vacancies tend to cluster together and are ordered to form a 4-unit-cell superstructure with $\vec{q}_0 = (\frac{1}{4}, 0, 0)$ along $\mathbf{a}^*$ direction. The superlattice consists of large anisotropic displacements of Cu, Ba, and O atoms, respectively and appears to be consistent with the presence of an O-ordered “Ortho-IV” phase. These “Ortho-IV” minority phase islands also induce long-range strains to the surrounding lattices, which manifest themselves as HDS observed in our experiments. Our quantitative analysis further revealed a $\mathbf{b}$ direction lattice modulation within the islands with the wavevector to be $\vec{q}_1 = (0, 0.21, 0)$. The fact that $\vec{q}_1$ is very close to the nesting vector connecting the nearly nested Fermi surface(FS) “ridges” originated from the metallic Cu-O chains strongly indicates that the $\mathbf{b}$ direction modulation is induced by the FS effect.

1

Introduction

The parent compounds of the copper oxide high temperature superconductors (cuprates) are the so-called Mott insulators where the strong electron-electron interactions prevent the electrons from hopping and the ground state is anti-ferromagnetic[11]. Superconductivity arises when they are doped away from stoichiometry by chemical substitution or adding or removing oxygen atoms. The dopants not only modify the electronic structures of the cuprates by contributing carriers to the CuO_2 planes but also introduce local disorder.

In most of the current theories, it is assumed that the dopant atoms only change the hole concentration but are otherwise passive players in the high temperature superconducting phenomena. The local disorder induced by the dopants, which would further complicate what is already hard theoretical problem, are generally ignored. In the cuprates the superconducting coherence length is short(of the order of tens of angstroms [12, 13]) and the local disorder is on a similar scale length. Thus, unlike the ordinary metals where the local impurity effect is screened by highly itinerant carries, in the cuprates the dopant induced local disorder might have more significant effect on the electronic properties.

Recently, remarkable nano-scale electronic inhomogeneities have been observed by scanning tunneling microscopy (STM) experiments on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ [14, 15], $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{CuO}_y$ [16] and $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ [17] compounds. In particular, the electronic inhomogeneities observed by STM manifests themselves as spatial variations in both the local density of states and the superconducting gaps. The spatial correlation between the variation of the gap width and the distribution of the dopants in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ revealed by McElroy *et al.* [15] links the observed electronic inhomogeneities to the dopant induced local disorders.

It has been suggested [14, 18, 19, 20] that the inhomogeneity originates from the poorly screened electrostatic potentials of the randomly distributed dopant atoms in these compounds. In this scenario, the effectively negatively charged dopant atoms attract nearby holes and create a higher local doping concentration with a smaller pairing gap [18, 19]. This interpretation leads to the prediction that the variation of the gap width and the distribution of the dopants should be spatially *negatively* correlated. However, the spatial correlation found in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ by McElroy *et al.* [15] is in the opposite direction. This discrepancy promotes the idea that the dopant induced local structural distortion (or local strain) may play a more important role [15, 21, 22, 23].

Whether the driving force for the observed inhomogeneity is of electronic origin or structural origin is still an open question. The experimental information on how and how much the dopants perturb the local lattice is crucial to clarify the problem. X-ray diffuse scattering is the ideal tool to study the nano-scale local structural distortions with the distortion amplitude to be of sub-angstrom due to its short wavelength and the high brilliance achievable at the third-generation synchrotron radiation sources. In this dissertation,

I will present our X-ray diffuse scattering experiment results on two cuprate compounds, $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ together with quantitative analysis.

The organization of the dissertation is as the following. In Chapter 2, the principles of X-ray scattering from single crystals are briefly reviewed. The basic concepts of X-ray diffraction are introduced in this chapter. In chapter 3, the theory of X-ray diffuse scattering from local structural disorder is discussed. Chapter 4 presents our X-ray diffuse scattering experiment results on $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$. Based on the X-ray diffuse scattering theory discussed in chapter 2, the local structural distortion pattern associated with the Sr dopants is reconstructed from experimental data. In chapter 5, our X-ray diffuse scattering experiment results on $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ compound are discussed together with their quantitative analysis. The modeling of the oxygen vacancy ordering in this compound is given in the appendix A.

2

Principles of X-ray scattering from single crystals

In this chapter, the principles of X-ray scattering from single crystals will be reviewed. Important concepts for single crystal X-ray scattering, such as atomic scattering factor, unit cell structure factor, reciprocal space and Bragg reflections will be introduced. Since we will focus on the studies of structural properties of single crystals, only the leading effect of high energy X-ray scattering, Thompson elastic scattering, will be discussed.

2.1 Atomic factor and structure factor

The elementary scattering unit for X-rays in materials is the electron. In the classic description, a free electron is forced to vibrate in the alternating electric field when sitting in an X-ray beam. When accelerated, the electron itself radiates as a source in all directions. The radiated field can be derived from Maxwell's equations. The scattering process becomes complicated when electrons are bound by nuclei to form atoms because many new quantum

electron states are formed. This complexity is further increased when atoms are regularly packed together to form crystals because the atomic quantum levels form bands. In addition, other elementary excitations, such as phonons, may be involved in the scattering process. The electrons can also be excited into new states with a change of energy, momentum and angular momentum. New effects, such as Raman scattering, resonant scattering, absorption, photoelectric effect *etc.* will occur. Since the X-ray is coupled to many degrees of freedom of the electrons, the X-ray scattering technique has been a powerful tool in the condensed matter research. Here, we will focus on the application of high energy X-ray scattering. When the X-ray energy is so high to be above all the transition edges, the X-ray scattering is not sensitive to phenomena involving real or virtual excitations. Rather, it can be well approximated as the interference of the scattering from individual electrons in the free electron approximation, which will reveal the crystal structural properties of the materials as shown in the following discussion. This is generally known as the elastic Thompson scattering.

2.1.1 X-ray scattering from single free electron

Classical theory and quantum mechanics provide equivalent descriptions of the Thompson scattering[24, 25] and the classical description will be followed here. The X-ray scattering from a electron is illustrated in Fig.(2.1), assuming an incident plane wave. The plane defined by the incident beam vector $\vec{k}_i$ and the scattered beam vector $\vec{k}_f$ is called the scattering plane. The X-ray beam can be split into σ and π channels with the electric field vector being perpendicular to or in the scattering plane. The amplitude of the electric vector of the scattered beam can be written in term of the incident beam electric vector

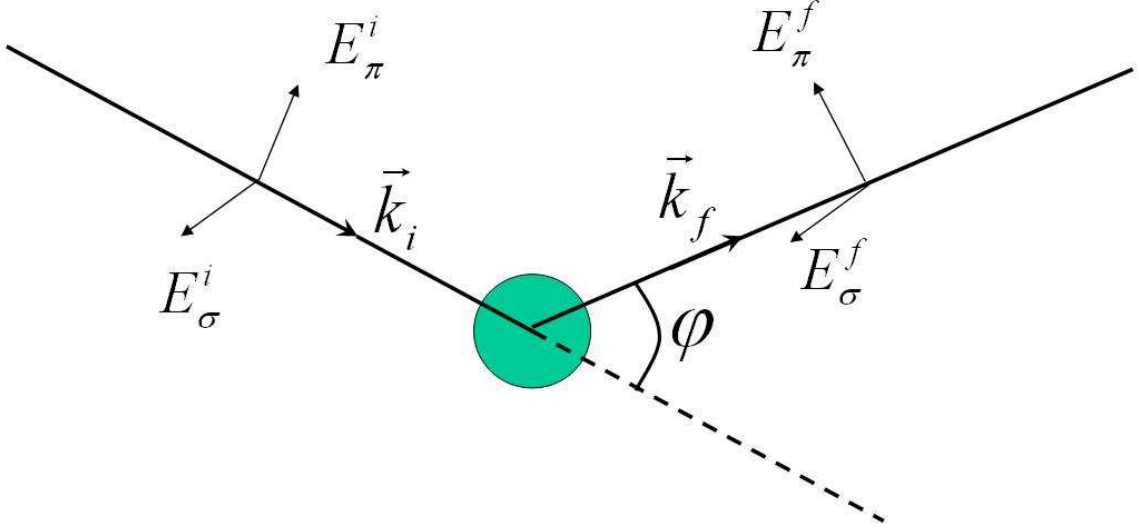


Figure 2.1 Schematic picture of the scattering of the unpolarized X-ray beam from single electron.

as[24, 25],

$$\begin{pmatrix} E_{\sigma}^f \\ E_{\pi}^f \end{pmatrix} = \frac{-e^2}{4\pi\epsilon_0 mc^2 R} \begin{pmatrix} E_{\sigma}^i \\ \cos \varphi E_{\pi}^i \end{pmatrix} \quad (2.1)$$

where R is the distance between the electron and the observation point. The constant part of the prefactor, $\frac{e^2}{4\pi\epsilon_0 mc^2}$, is also called *classical electron radius*, which is denoted as r_0 and $r_0 = 2.82 \times 10^{-5} \text{Å}$. Eqn.(2.1) shows that, for Thompson scattering, the σ and π channels are totally separated from each other. Usually, the experiments designed to study the structural properties of single crystals cover a broad range of φ angle. The $\cos \varphi$ factor in the π channel scattering complicates the data analysis. All the experiments which will be presented in this dissertation were performed at synchrotron sources, where the incident X-ray beam is polarized into σ channel which has no φ angle dependence in Eqn.(2.1). All the following discussions will be restricted to the σ - σ channel scattering.

2.1.2 X-ray scattering from single atom

An atom can be viewed as a nucleus surrounded by electron cloud. The density of the electron cloud is denoted as $\rho(\vec{r})$. The scattered X-ray beam is the superposition of the scattering contributions from different volume elements of the electron cloud, as shown in Fig(2.2). The sketch in Fig(2.2) already carries the far field approximation[24] which says that, when the X-ray source and the observation point are at distances very large compared with the dimension of the illuminated sample region, both the incident beam and the scattered beam can be well approximated as plane wave. The phase difference between the scattering from the two volume elements sitting $\vec{r}$ away from each other is,

$$\Delta\phi(\vec{r}) = (\vec{k}_i - \vec{k}_f) \cdot \vec{r} \quad (2.2)$$

At the observation point, the electric field of the scattered X-ray beam from an atom is the interference result of all volume elements as,

$$E_f = -\frac{r_0}{R} E_0 e^{i\phi_0} \int_{\vec{r}} \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}^3 \quad (2.3)$$

where E_0 is the amplitude of the incident beam and ϕ_0 is a constant phase term for the origin point of the coordinate which is determined by instrument setup and unrelated to the scattering object. In Eqn.(2.3), we introduce a very important quantity for X-ray scattering, $\vec{Q}$, namely the *wave vector transfer*, defined as

$$\vec{Q} = \vec{k}_i - \vec{k}_f \quad (2.4)$$

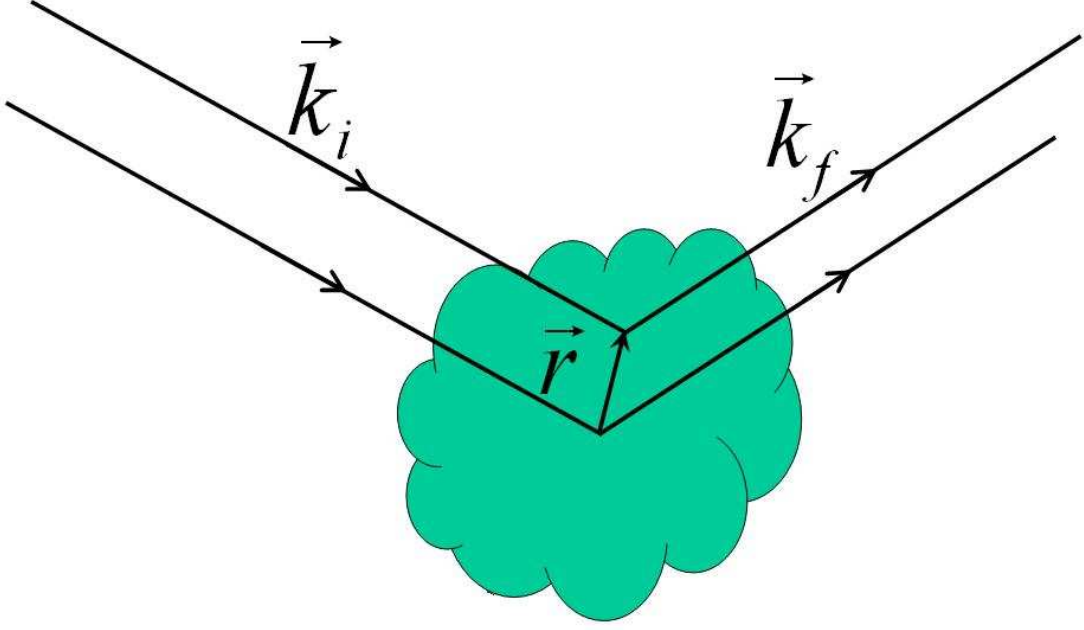


Figure 2.2 Schematic picture of the scattering of the X-ray beam from the electron cloud of an atom.

The amplitude of Thompson scattering can thus be viewed as the Fourier transform of the real space electron density distribution in $\vec{Q}$ space, or reciprocal space in the language of crystallography. The integration in Eqn.(2.3), $\int_{\vec{r}} \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$, is related to the property of the atoms and is often called *atomic scattering factor*, denoted as $f^0(\vec{Q})$.

Since for elastic scattering $k_i = k_f$, from Eqn.(2.4), we have the relation $Q = 2k \sin \theta$ where θ is half of the angle between $\vec{k}_i$ and $\vec{k}_f$. In the limit that $Q \rightarrow 0$, which is the forward scattering condition when $\theta \rightarrow 0$, all of the different volume elements scatter in phase so that $f^0(\vec{Q} = 0) = Z$, the number of electrons in the atom. For single crystal structural studies, hard X-rays are employed to get good penetration into the samples and because Q needs to be large to reach out far enough in the reciprocal space. For example, for the scattering of 20KeV X-rays at $\theta = 20$ degrees, $Q = 6.9 \text{ \AA}^{-1}$. Since the typical radius of atoms are $\sim \text{\AA}$, the phase variation in the integration of Eqn.(2.3) is large and

the $\vec{Q}$ -dependence of the atomic scattering factor must be taken into account. Usually, the approximation of spherical symmetry for the electron cloud density is used to further simplify the expression for the atomic form factor $f^0(\vec{Q})$. With this approximation, the electron density, $\rho(\vec{r})$, can be written as $\rho(r)$ and $f^0(\vec{Q})$ is,

$$f^0(\vec{Q}) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin Qr}{Qr} dr \quad (2.5)$$

Even though the spherical symmetry approximation is not exactly true, it describes the electron cloud with reasonably high accuracy because the electrons sitting in the closed shells of atoms do have spherical symmetry and they are the majority of the electrons of most of the atoms, especially for those have high Z values. An important consequence of the spherical symmetry approximation is that the imaginary part of the integration, $\int_{\vec{r}} \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$, becomes zero and $f^0(\vec{Q})$ is a pure real number. In principle, there would be an anomalous imaginary part of $f^0(\vec{Q})$ when the X-ray energy is close to one of the absorption edges. In this dissertation, all experiments were done with hard X-rays, whose energies were way above all transition edges, and the absorption effect will not be considered here. Further evaluation of $f^0(\vec{Q})$ needs detailed information of $\rho(\vec{r})$. $f^0(\vec{Q})$ for Z from 0 to 100 has been tabulated in the International Tables[26].

2.2 Scattering from ideal crystals

When the constituent atoms are bonded and packed in a regularly ordered, repeating pattern extending in all three spatial dimensions, crystals are formed. The basis repeating elements are called unit cells and the basis vectors of the repeating unit cell are

denoted as $(\mathbf{a}, \mathbf{b}, \mathbf{c})$. Then, The position of the l -th unit cell can be written as,

$$\vec{R}_l = l_1 \mathbf{a} + l_2 \mathbf{b} + l_3 \mathbf{c} \quad (2.6)$$

where l stands for the triplet of 3 integers (l_1, l_2, l_3) . We index the atoms inside an unit cell with k and denote the position of the k -th atom inside the l -th unit cell as $\vec{R}_{lk} = \vec{R}_l + \vec{R}_k$ where $\vec{R}_k$ is the “average” position of the k -th atom relative to the unit cell center. The term “average” is used because the atoms never stay at fixed positions. At finite temperatures, T , the atoms are vibrating around the “average” positions due to thermal excitation. Even at $T = 0$, there is zero-point motion due to quantum fluctuations.

2.2.1 Bragg reflection from perfect “static” single crystals

The electric field due to Thompson X-ray scattering from a single crystal is the superposition of the contribution from all the atoms,

$$E_f = -\frac{r_0}{R} E_0 e^{i\phi_0} \sum_{lk} f_k^0(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_{lk}} \quad (2.7)$$

X-ray detectors usually count single photons and the measured intensity, I_f , is then the number of photons per second recorded by the detectors, which is proportional to the energy per unit area and the total area subtended by the detectors. With the total detector area written in terms of solid angle $\Delta\Omega$, the I_f can be written as,

$$I_f \propto |E_f|^2 R^2 \Delta\Omega = |r_0 E_0|^2 \Delta\Omega \left| \sum_{lk} f_k^0(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_{lk}} \right|^2 \quad (2.8)$$

Since the incident X-ray intensity, I_0 , is proportional to $|E_0|^2$ and the cross sectional area of the beam A_0 , we have,

$$\frac{I_f A_0}{I_0 \Delta \Omega} = r_0^2 \left| \sum_{lk} f_k^0(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_{lk}} \right|^2 \quad (2.9)$$

The left hand side of the equation is also known as the *differential cross-section*, which is often denoted as $d\sigma/d\Omega$,

$$\frac{d\sigma}{d\Omega} = \frac{I_f}{(I_0/A_0)\Delta\Omega} = \frac{(\text{Number of X-rays scattered per second into } \Delta\Omega)}{(\text{Incident flux})(\Delta\Omega)} \quad (2.10)$$

Since the I_0/A_0 and $\Delta\Omega$ are determined by instrumental setup and unrelated to the sample properties, they just affect the final scaling of the measured intensity. Thus, Eqn.(2.9) can be simplified by assuming I_0/A_0 and $\Delta\Omega$ are unity. Then, we write the normalized scattered intensity in *electron units* as,

$$I = \left| \sum_{lk} f_k^0(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_{lk}} \right|^2 \quad (2.11)$$

Eqn.(2.11) is the most commonly used equation in single crystal X-ray scattering. Putting the perfect crystal condition for $\vec{R}_{lk}$ as defined in Eqn.(2.6) into Eqn.(2.11), we obtain the so called Bragg reflection,

$$I = \left| \sum_k f_k^0(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_k} \right|^2 \left| \sum_{l_1 l_2 l_3} e^{i\vec{Q} \cdot (l_1 \mathbf{a} + l_2 \mathbf{b} + l_3 \mathbf{c})} \right|^2 \quad (2.12)$$

The first summation is over all the atoms within an unit cell and is called the *structure factor* of the unit cell. Since l_1 , l_2 and l_3 are integers, the second summation is non-zero

only when $\vec{Q} = n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*$ where (n_1, n_2, n_3) are integers and $(\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$ defined as,

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})}, \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})} \quad (2.13)$$

and they are called *reciprocal lattice basis vectors*. $\vec{Q} = n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*$ is called the Bragg condition and the $\vec{Q}$ satisfying the Bragg condition is often denoted as $\vec{G}$, known as the “Bragg point”. The set of $\vec{G}$ s form a lattice in three dimensional reciprocal space, known as the reciprocal lattice. Conventionally, the Bragg peaks are labeled with Miller index $[h, k, l]$ in unit of $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$, called reduced lattice units(r.l.u.). Also, any points in the reciprocal space can be denoted in r.l.u. as $\vec{Q} = (h, k, l)$.

2.2.2 Thermal diffuse scattering

With thermal excitation, extra terms are needed to describe the positions of the atoms inside a single crystal. By introducing $\vec{u}_{lk}$, the extra displacement due to thermal vibrations, the instantaneous atom positions become $\vec{R}_{lk} + \vec{u}_{lk}$ and Eqn.(2.11) is rewritten as,

$$I = \left\langle \left| \sum_{lk} f_k^0(\vec{Q}) e^{i\vec{Q} \cdot (\vec{R}_{lk} + \vec{u}_{lk})} \right|^2 \right\rangle = \sum_{ll'kk'} f_k^0(\vec{Q}) f_{k'}^{0*}(\vec{Q}) e^{i\vec{Q} \cdot (\vec{R}_{lk} - \vec{R}_{l'k'})} \langle e^{i\vec{Q} \cdot (\vec{u}_{lk} - \vec{u}_{l'k'})} \rangle \quad (2.14)$$

The angle brackets $\langle \dots \rangle$ indicates a temporal average because the vibration $\vec{u}_{lk}$ is of a function of time. The result of the averaging is[24],

$$\langle e^{i\vec{Q} \cdot (\vec{u}_{lk} - \vec{u}_{l'k'})} \rangle = e^{-\frac{1}{2} \langle (\vec{Q} \cdot \vec{u}_{lk})^2 \rangle} e^{-\frac{1}{2} \langle (\vec{Q} \cdot \vec{u}_{l'k'})^2 \rangle} e^{\langle (\vec{Q} \cdot \vec{u}_{lk}) (\vec{Q} \cdot \vec{u}_{l'k'}) \rangle} \quad (2.15)$$

The $e^{-\frac{1}{2}\langle(\vec{Q}\cdot\vec{u}_{lk})^2\rangle}$ is actually independent of the index l and is known as the Debye-Waller factor for the k -th atom, which is usually denoted as e^{-W_k} . In the following discussion, we will combine the Debye-Waller factor with $f_k^0(\vec{Q})$ with a new notation, $\tilde{f}_k = e^{-\frac{1}{2}\langle(\vec{Q}\cdot\vec{u}_{lk})^2\rangle} f_k^0(\vec{Q})$ whose $\vec{Q}$ -dependence will not be specified anymore.

If the temperature is not extremely high, $\langle(\vec{Q}\cdot\vec{u}_{lk})(\vec{Q}\cdot\vec{u}_{l'k'})\rangle$ can be treated as small quantity for most crystals. By expanding $e^{\langle(\vec{Q}\cdot\vec{u}_{lk})(\vec{Q}\cdot\vec{u}_{l'k'})\rangle}$ and keep the terms up to the first order,

$$e^{\langle(\vec{Q}\cdot\vec{u}_{lk})(\vec{Q}\cdot\vec{u}_{l'k'})\rangle} = 1 + \langle(\vec{Q}\cdot\vec{u}_{lk})(\vec{Q}\cdot\vec{u}_{l'k'})\rangle \quad (2.16)$$

Then the total scattered intensity can be written as,

$$I = \left| \sum_{lk} \tilde{f}_k e^{i\vec{Q}\cdot\vec{R}_{lk}} \right|^2 + \left\langle \left| \sum_{lk} \tilde{f}_k \vec{Q} \cdot \vec{u}_{lk} e^{i\vec{Q}\cdot\vec{R}_{lk}} \right|^2 \right\rangle \quad (2.17)$$

The first term is similar to Eqn.(2.11) and will also give rise to the Bragg peaks, except that the intensities of the Bragg peaks will be reduced due to the Debye-Waller factors. The second term is known as Thermal Diffuse Scattering(TDS). As the result of thermal excitation, $\vec{u}_{lk}$ can be written as the superposition of the excitation of the phonon modes[27],

$$\vec{u}_{lk} = \left(\frac{\hbar}{2NM_k} \right)^{1/2} \sum_{\vec{q}j} \frac{\hat{e}(k|\vec{q}j)}{\omega_j(\vec{q})^{1/2}} e^{i\vec{q}\cdot\vec{R}_l} A_{\vec{q}j} \quad (2.18)$$

where N is the total number of unit cells and M_k is the mass of the k -th atom. $\hat{e}(k|\vec{q}j)$ and $\omega_j(\vec{q})$ are the eigenvector and eigenvalue for the j -th phonon mode at wavevector $\vec{q}$, respectively. $A_{\vec{q}j}$ is called the phonon field operator and can be expressed in term of phonon creation and annihilation operators as $A_{\vec{q}j} = a_{\vec{q}j} + a_{-\vec{q}j}^\dagger$.

With the expansion of $\vec{u}_{lk}$ on the basis of phonon modes, the intensity of TDS,

I_{TDS} , becomes,

$$I_{TDS} = \frac{N\hbar}{2} \sum_{kk'j} \tilde{f}_k \tilde{f}_{k'} e^{i\vec{G} \cdot (\vec{R}_k - \vec{R}_{k'})} \frac{\vec{Q} \cdot \hat{e}(k|\vec{q}j) \vec{Q} \cdot \hat{e}(k'|\vec{q}j)}{\sqrt{M_k M_{k'}} \omega_j(\vec{q})} \coth \frac{\hbar \omega_j(\vec{q})}{2KT} \quad (2.19)$$

where $\vec{G}$ is the nearest Bragg point to $\vec{Q}$ and we have the relation: $\vec{q} = \vec{Q} - \vec{G}$. In low q region, the frequency $\omega_j(\vec{q})$ for optical phonon modes are much larger than that of the acoustic modes. With $\omega_j(\vec{q})$ as a denominator in Eqn.(2.19), the contribution from optical phonon modes is very small. Further, the thermal population factor, $\coth \frac{\hbar \omega_j(\vec{q})}{2KT}$, is also small for the optical phonon modes. Thus, the overall contribution to the HDS from optical phonon modes can be ignored in most cases.

With only the acoustic considered, Eqn.(2.19) can be further simplified by approximating the acoustic modes with continuum elastic theory which describes the acoustic modes very well at low q region and is theoretically much simpler. Detailed transformation from rigorous lattice dynamics analysis to continuum elastic theory treatment is discussed in Chapter 3. With continuum elastic theory, the TDS from acoustic phonon can be written as,

$$I_{TDS}(Q) = \frac{N\hbar}{2M} \left| \sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} \right|^2 \sum_j \frac{[\vec{Q} \cdot \tilde{e}(\vec{q}j)]^2}{\omega(\vec{q}j)} \coth \frac{\hbar \omega(\vec{q}j)}{2KT} \quad (2.20)$$

where $\tilde{e}(\vec{q}j)$ is the eigenvector for Eqn.(3.9) with the elastic dynamic matrix defined there.

The orthonormality and closure conditions for $\tilde{e}(\vec{q}j)$ are,

$$\sum_{\alpha} \tilde{e}_{\alpha}^*(\vec{q}j) \tilde{e}_{\alpha}(\vec{q}j') = \delta_{jj'} \quad \text{and} \quad \sum_j \tilde{e}_{\beta}^*(\vec{q}j) \tilde{e}_{\alpha}(\vec{q}j) = \delta_{\alpha\beta} \quad (2.21)$$

3

X-ray diffuse scattering from non-ideal single crystals

For real crystals, the crystal structures can deviate from perfect periodicity due to various reasons. For High Temperature superconducting cuprates, the class of materials interested in this dissertation, the crystal structures are inevitably perturbed by the chemically introduced dopants. The very short wavelength (comparable with the interatomic distances) of X-rays makes the X-ray diffraction a very powerful tool for studying imperfections in crystals. In this chapter, the theory of X-ray diffuse scattering from local lattice distortion and short range ordering will be reviewed.

3.1 General principles of X-ray diffuse scattering from perturbed crystal structure

When the crystal structure is perturbed, the perfect crystal condition (Eqn.(2.6)) is not satisfied anymore and extra displacement terms, u_{lk} need to be introduced,

$$I = \langle \left| \sum_{lk} \tilde{f}_k e^{i\vec{Q} \cdot (\vec{R}_{lk} + \vec{u}_{lk})} \right|^2 \rangle \quad (3.1)$$

The extra displacements u_{lk} for the perturbed crystal can have different origins and properties. Apart from the lattice vibrations due to thermal excitations introduced in the previous chapter, for the cuprate families, it can have a well ordered long range lattice modulation, such as the superstructure in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [28, 29]; or have only a short range ordered lattice modulation, such as the multi structural phases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [30]; or arise from randomly distributed dopant atoms, such as the strain fields in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

3.2 Super structure peaks from ordered lattice modulation

There are two types of ordered periodic lattice modulations, commensurate or incommensurate. Here we will concentrate on the commensurate lattice modulation since the multi structural phases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, one of the two cuprate families studied in this dissertation, are of this type. When commensurate superlattice structure develops, we have $\vec{u}_{lk} = \vec{u}_{(l+l^0)_k}$ with $l^0 \equiv (l_1^0, l_2^0, l_3^0)$. The three elements for the unit cell index are integers and along the three unit cell vector directions, respectively. With this periodicity, $\vec{u}_{lk}$ can

be re-indexed as $\vec{u}_{mnk}$ and,

$$l = (m_1 l_1^0, m_2 l_2^0, m_3 l_3^0) + (n_1, n_2, n_3), \quad n_j < l_j^0 \quad (3.2)$$

where $m \equiv (m_1, m_2, m_3)$, denoting a supercell index and $n \equiv (n_1, n_2, n_3)$ is the index of the unit cells within a supercell. Since $\vec{u}_{lk} = \vec{u}_{(l+l^0)_k}$, it does not depend on the index m and can be written as $\vec{u}_{nk}$. With the new index, the unperturbed original atom position, $\vec{R}_{lk}$ can be split into three components, $\vec{R}_m + \vec{R}_n + \vec{R}_k$, and,

$$\vec{R}_m = m_1 l_1^0 \mathbf{a} + m_2 l_2^0 \mathbf{b} + m_3 l_3^0 \mathbf{c}, \quad \vec{R}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (3.3)$$

Thus, the total X-ray scattering intensity can be written as,

$$I = \langle \left| \sum_{lk} \tilde{f}_k e^{i\vec{Q} \cdot (\vec{R}_{lk} + \vec{u}_{lk})} \right|^2 \rangle = \left| \sum_{nk} \tilde{f}_k e^{i\vec{Q} \cdot (\vec{R}_{nk} + \vec{u}_{nk})} \right|^2 \left| \sum_m e^{i\vec{Q} \cdot \vec{R}_m} \right|^2 \quad (3.4)$$

which is similar to Eqn.(2.12) except that the unit cell structure factor there becomes the superstructure factor. Analogous to Eqn.(2.12), the second summation also gives non-zero values at certain points in reciprocal space such as $\vec{Q} = (j_1/l_1^0, j_2/l_2^0, j_3/l_3^0)$ in r.l.u.. We can see that in between the original Bragg peaks of the unperturbed crystal where the three components of $\vec{Q}$ are integers in r.l.u., new peaks appear and the spacing of the new peaks is determined by the modulation periodicity l^0 . The relative intensities of the new superstructure peaks to the original Bragg peaks are determined by the superstructure factor. When $\vec{u}_{lk}$ are small, the scattering from the unit cells within a super cell is still close to in-phase at Bragg points and destructive at the new peak positions. Thus the new

peaks are much weaker than the Bragg peaks and are called diffuse superstructure peaks. When $\vec{u}_{lk}$ are large, the above argument does not hold and, for an extreme case where the $\vec{u}_{lk}$ is very large, we essentially end up with a totally new crystal structure. This is the case when a structural phase transition occurs.

When the ordered modulation is of short range rather than the long range scenario discussed above, more factors need to be considered, such as the effective volume where the short range order modulation forms and the correlation lengths of the short range order, etc. The situation can be different for different types of short range order and the special case of short range oxygen vacancy ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ will be discussed in detail in Chapter 5.

3.3 X-ray diffuse scattering due to point-like defects

When defects, such as dopant atoms, are randomly distributed, they will introduce local strain to the surrounding crystal lattice usually due to the size misfit. The associated lattice distortion, centered around the defects, will give rise to diffuse scattering patterns around the Bragg peaks with special symmetries and properties, which is known as Huang Diffuse Scattering(HDS)[31]. By measuring and quantitatively analyzing the HDS, the local lattice distortion introduced by the defects can be examined. The diffuse scattering from crystals containing defects with displacements has been first calculated by P.Eckstein[32] and K.Huang[31]. The theory of HDS was later on further developed and generalized by H.Kanzaki[33], P.H.Dederichs[34] and W.A.Krivoglaz[35]. In Krivoglaz's book[35], various defects have been classified into two classes. In this thesis, we will focus on "First-Class Defects" which have low concentration in the crystals and introduce weak lattice distortions.

3.3.1 Lattice distortions due to the defects

For a perfect crystal, the equation of motion of the lattice within the harmonic approximation can be written as,

$$\mathcal{F}_{lk\alpha} = M_k \ddot{u}_{lk\alpha} = - \sum_{l'k'\beta} \Phi_{\alpha\beta}^{lk'l'k'} u_{l'k'\beta} \quad (3.5)$$

where $\vec{u}_{lk}$ is the displacement of the k -th atom in the l -th unit cell from its equilibrium position and M_k is its mass. The coefficients $\Phi_{\alpha\beta}^{lk'l'k'}$, which are the second derivatives of the total crystal potential energy with respect to the atomic displacements in the equilibrium configuration, are called *atomic force constants*. Thus, $\vec{\mathcal{F}}_{lk}$ is the force exerted on the k -th atom in the l -th unit cell by other displaced atoms in the crystal. The displacement can be caused by various reasons, for example, thermal phonon excitation. If we replace each $\vec{u}_{lk}$ by $\vec{v}$ we have merely displaced the lattice rigidly through the vector $\vec{v}$, and this operation will not change the value of the force on an atom in the initial configuration. We thus have the condition,

$$\sum_{l'k'} \Phi_{\alpha\beta}^{lk'l'k'} = 0 \quad (3.6)$$

This important property of the atomic force constants will be used in later on discussion.

When defects are introduced in to a single crystal, they vary the local crystal potential. This effect can be viewed as extra forces introduced by the defects to the surrounding atoms, known as “Kanzaki force” named after H.Kanzaki[33]. Regarding the lattice distortion associated with the dopants, the crystal can be divided into two regions. Since the Kanzaki force from the dopants decreases rapidly as a function of distance[33], only the nearest and the second nearest unit cells are distorted directly by the Kanzaki force

and unit cells further away from the dopants are not affected that much by it. However, they will also be distorted through elastic coupling with the displaced nearest and the next nearest unit cells to accommodate the very local lattice distortion directly caused by the Kanzaki force. Thus, the lattice distortion propagates out as a long range strain field. This scenario of lattice distortion due to the dopants is schematically presented in Fig.(3.1).

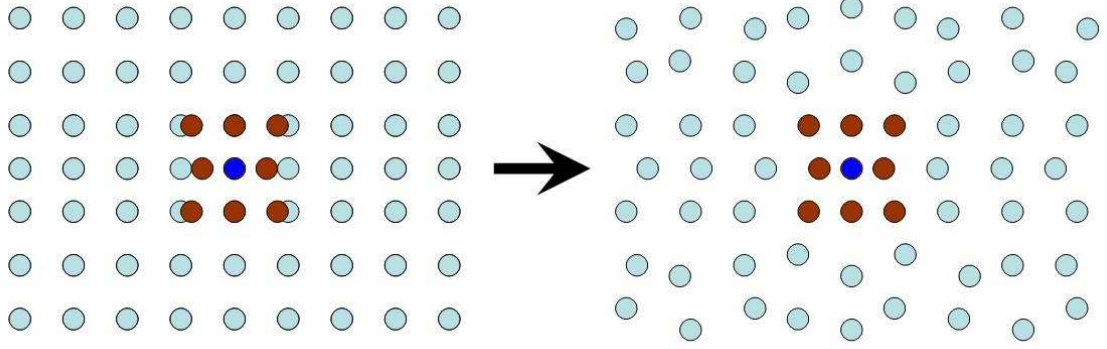


Figure 3.1 Schematic picture of the lattice distortion due to single defect in primitive crystals. Blue: the defect; Red: the nearest and the second nearest atoms. Left: Kanzaki force causes very local distortion directly. Right: the very local distortion propagates out through elastic lattice coupling.

As a result, the lattice is distorted to balance the Kanzaki force and the relation between lattice distortion vector $\vec{u}_{lk}$ and Kanzaki force $\vec{F}_{lk}$ is,

$$F_{lk\alpha} = \sum_{l'k'\beta} \Phi_{\alpha\beta}^{lkl'k'} u_{l'k'\beta} \quad (3.7)$$

If the temperature is not extremely high, the dopants are immobile and thus, the associated lattice distortions are static.

3.3.2 Lattice motion and phonon modes

In principle, we can solve for lattice distortion vector $\vec{u}_{lk}$ in term of the Kanzaki force $\vec{F}_{lk}$ from Eqn.(3.7) and treat the Kanzaki forces as fitting parameters in the quanti-

tative analysis of the X-ray diffuse scattering data. The transformation of Eqn.(3.7) will be done by expanding $\vec{u}_{lk}$ in the phonon modes in the following discussion. Since some of the properties of phonon modes will be employed in the derivation, we quickly review them here.

Due to the periodicity of the lattice, the atomic force constants, $\Phi_{\alpha\beta}^{lk'l'k'}$, do not depend on the specific pair of unit cells (l, l') but only depend on their relative position $(l - l')$ [27]. Taking the advantage of this property, Eqn.(3.5) can be simplified by choosing as a solution of the form,

$$u_{lk\alpha} = A \frac{e_{k\alpha}}{\sqrt{M_k}} e^{-i\omega t + i\vec{q} \cdot \vec{R}_{lk}} \quad (3.8)$$

where $\vec{e}_k$ is independent of l and A is an amplitude factor. Substitute this expression into Eqn.(3.5) we find that,

$$\omega^2 e_{k\alpha} = \sum_{k'\beta} D_{\alpha\beta}^{kk'}(\vec{q}) e_{k'\beta} \quad (3.9)$$

where the elements of the matrix $D(\vec{q})$, called *dynamical matrix*, are given by,

$$D_{\alpha\beta}^{kk'}(\vec{q}) = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{l'} \Phi_{\alpha\beta}^{lk'l'k'} e^{-i\vec{q} \cdot (\vec{R}_{lk} - \vec{R}_{l'k'})} \quad (3.10)$$

Thus, Eqn.(3.5) has been reduced to the problem of solving a set of $3r$ (r is the total number of atoms in an unit cell) linear homogeneous equations in $3r$ unknowns, the $\vec{e}_k$. The $3r$ set of eigenvectors and associated eigenvalues with certain $\vec{q}$ value are the phonon polarization vectors and squares of the phonon frequencies respectively and will be denoted as $\vec{e}_k(\vec{q}j)$

and $\omega_{\vec{q}j}^2$ with $j = 1, 2, \dots, 3r$. Then Eqn.(3.5) can be written as,

$$M_k \omega_{\vec{q}j}^2 \frac{e_{k\alpha}(\vec{q}j)}{\sqrt{M_k}} e^{i\vec{q} \cdot \vec{R}_{lk}} = \sum_{l'k'\beta} \Phi_{\alpha\beta}^{lk'l'k'} \frac{e_{k'\beta}(\vec{q}j)}{\sqrt{M_{k'}}} e^{i\vec{q} \cdot \vec{R}_{l'k'}} \quad (3.11)$$

We see that $\vec{e}_k(\vec{q}j)$ is defined with a constant factor. We can choose this factor in such a way that $\vec{e}_k(\vec{q}j)$ satisfies the orthonormality and closure conditions

$$\sum_{k\alpha} e_{k\alpha}^*(\vec{q}j) e_{k\alpha}(\vec{q}j') = \delta_{jj'}, \quad \sum_j e_{k'\beta}^*(\vec{q}j) e_{k\alpha}(\vec{q}j) = \delta_{\alpha\beta} \delta_{kk'} \quad (3.12)$$

3.3.3 Phonon modes expansion of the lattice distortion

As the eigen solutions to the equation of motion of the lattice(Eqn.(3.5)), the phonon modes form a set of complete basis for any lattice distortions, assuming the distortion is small and the harmonic approximation holds. Thus, we can expand the displacements $\vec{u}_{lk}$ on the basis of phonon modes as,

$$u_{lk\alpha} = \sum_{\vec{q},j} A_{\vec{q}j} \frac{e_{k\alpha}(\vec{q}j)}{\sqrt{M_k}} e^{i\vec{q} \cdot \vec{R}_{lk}} \quad (3.13)$$

where $\vec{e}(\vec{q}j)$ is the eigenvector of the j -th phonon mode with the wavevector $\vec{q}$. $A_{\vec{q}j}$ is the amplitude coefficient of the j -th phonon mode with the wavevector $\vec{q}$ for the expansion. Substituting the expansion of $\vec{u}_{lk}$ into Eqn.(3.7), we get,

$$F_{lk\alpha} = \sum_{\vec{q},j} A_{\vec{q}j} \left(\sum_{l'k'\beta} \Phi_{\alpha\beta}^{lk'l'k'} \frac{e_{k'\beta}(\vec{q}j)}{\sqrt{M_{k'}}} e^{i\vec{q} \cdot \vec{R}_{l'k'}} \right) \quad (3.14)$$

From Eqn.(3.11), the above equation can be readily written as,

$$F_{lk\alpha} = \sum_{\vec{q},j} A_{\vec{q}j} M_k \omega_{\vec{q}j}^2 \frac{e_{k\alpha}(\vec{q}j)}{\sqrt{M_k}} e^{i\vec{q} \cdot \vec{R}_{lk}} \quad (3.15)$$

Next, we will write the amplitude coefficients, $A_{\vec{q}j}$, in term of $\vec{F}_{lk}$ using the orthonormality of $\vec{e}_k(\vec{q}j)$. With Eqn.(3.15), we have,

$$\sum_{lk\alpha} F_{lk\alpha} \frac{e_{k\alpha}^*(\vec{q}'j')}{\sqrt{M_k}} e^{-i\vec{q}' \cdot \vec{R}_{lk}} = \sum_{lk\alpha} \left(\sum_{\vec{q},j} A_{\vec{q}j} M_k \omega_{\vec{q}j}^2 \frac{e_{k\alpha}(\vec{q}j)}{\sqrt{M_k}} e^{i\vec{q} \cdot \vec{R}_{lk}} \right) \frac{e_{k\alpha}^*(\vec{q}'j')}{\sqrt{M_k}} e^{-i\vec{q}' \cdot \vec{R}_{lk}} \quad (3.16)$$

The summation of unit cell index l on the right hand side imposes the selection of $\vec{q} = \vec{q}'$ and gives a constant N which is total number of unit cells. We find that,

$$\sum_{lk\alpha} F_{lk\alpha} \frac{e_{k\alpha}^*(\vec{q}'j')}{\sqrt{M_k}} e^{-i\vec{q}' \cdot \vec{R}_{lk}} = N \sum_j A_{\vec{q}j} \omega_{\vec{q}j}^2 \sum_{k\alpha} e_{k\alpha}(\vec{q}j) e_{k\alpha}^*(\vec{q}'j') \quad (3.17)$$

Applying the orthonormality condition of $\vec{e}_k(\vec{q}j)$ as in Eqn.(3.12), the second summation on the right hand side becomes $\delta_{jj'}$. As a result, we get,

$$A_{\vec{q}j} = \frac{1}{N} \sum_{lk\alpha} F_{lk\alpha} \frac{e_{k\alpha}^*(\vec{q}j)}{\omega_{\vec{q}j}^2 \sqrt{M_k}} e^{-i\vec{q} \cdot \vec{R}_{lk}} \quad (3.18)$$

Substituting this expression into Eqn.(3.13), we finally achieve the goal of expressing the lattice displacements $\vec{u}_{lk}$ in term of the Kanzaki force $\vec{F}_{lk}$ as,

$$u_{lk\alpha} = \frac{1}{N} \sum_{\vec{q},j} \left(\sum_{l'k'\beta} F_{l'k'\beta} \frac{e_{k'\beta}^*(\vec{q}j)}{\omega_{\vec{q}j}^2 \sqrt{M_{k'}}} e^{-i\vec{q} \cdot \vec{R}_{l'k'}} \right) \frac{e_{k\alpha}(\vec{q}j)}{\sqrt{M_k}} e^{i\vec{q} \cdot \vec{R}_{lk}} \quad (3.19)$$

3.3.4 Huang Diffuse Scattering from a single defect

To evaluate the X-ray diffuse scattering from the lattice distortion induced by a single defect, we again start with Eqn.(3.1). As mentioned at the beginning of the section, we will focus on the “First-Class Defects” which have low concentration in the crystals and introduce weak lattice distortions. With this condition, it is reasonable to assume that the lattice distortion $\vec{u}_{lk}$ is small. Thus we can expand the exponential $e^{i\vec{Q}\cdot\vec{u}_{lk}}$ and keep the terms up to the first order. With this linear approximation, Eqn.(3.1) can be written as,

$$I = \left| \sum_{lk} \tilde{f}_k e^{i\vec{Q}\cdot\vec{R}_{lk}} + i \sum_{lk\alpha} \tilde{f}_k Q_\alpha u_{lk\alpha} e^{i\vec{Q}\cdot\vec{R}_{lk}} \right|^2 \quad (3.20)$$

The first term gives rise to the regular Bragg reflection and the modulus squared of the second term produces the HDS pattern. Since the amplitude of the first term is sharply localized on Bragg points $\vec{G}$, the interference of the two terms is also well confined within the Bragg peak profile and does not contribute to the diffuse scattering. Considering the result we get from the previous section where $\vec{u}_{lk}$ is expressed in term of the Kanzaki force $\vec{F}_{lk}$, we can write the diffuse scattering intensity, I_{HDS} , as,

$$I_{HDS} = \frac{1}{N^2} \left| i \sum_{k\alpha} \tilde{f}_k Q_\alpha \sum_{\vec{q},j} \sum_{l'k'\beta} F_{l'k'\beta} \frac{e_{k\alpha}(\vec{q}j) e_{k'\beta}^*(\vec{q}j)}{\omega_{\vec{q}j}^2 \sqrt{M_k M_{k'}}} e^{-i\vec{q}\cdot\vec{R}_{l'k'}} \sum_l e^{i(\vec{Q}+\vec{q})\cdot\vec{R}_{lk}} \right|^2 \quad (3.21)$$

Again, the last summation on the unit cell index l imposes the selection of $\vec{Q} + \vec{q} = \vec{G}$ and the summation result is N if the relation is satisfied. Otherwise, it is zero. Thus, we find that,

$$I_{HDS} = \left| i \sum_{k\alpha} \tilde{f}_k e^{i\vec{G}\cdot\vec{R}_k} Q_\alpha \sum_j \sum_{l'k'\beta} F_{l'k'\beta} \frac{e_{k\alpha}(\vec{q}j) e_{k'\beta}^*(\vec{q}j)}{\omega_{\vec{q}j}^2 \sqrt{M_k M_{k'}}} e^{-i\vec{q}\cdot\vec{R}_{l'k'}} \right|^2 \quad (3.22)$$

To obtain Eqn.(3.22), only the harmonic lattice and small u_{lk} displacement approximations are made so far, which are applicable to most of the cases of the defect-induced lattice distortions. Thus, the HDS should be well described by a set of Kanzaki forces. But, it is impractical to treat the whole set of the Kanzaki forces as parameters in a quantitative analysis or fitting procedure because, in principle, the sub-index of $\vec{F}_{lk}$ runs over the whole crystal. Thus, a further approximation is needed to simplify Eqn.(3.22).

From Eqn.(3.18), we can tell that the amplitude of the optical-type components of the lattice distortion is much smaller than the amplitude of the acoustic-type components with the denominator ω_{qj}^2 , because ω_{qj} of the optical phonon branches can be several times or even orders of magnitude larger than that of the acoustic phonon branches, especially in the small q region. This denominator is carried into Eqn.(3.22) for the intensity of HDS. Thus, another approximation, namely the acoustic approximation is usually employed to simplify Eqn.(3.22), where the optical-type components of the lattice distortion will be neglected and the summation of index j will run from $j = 1$ to 3 for the three acoustic modes.

Also, as discussed in Section 3.3.1, since the Kanzaki force decreases rapidly as a function of distance from the dopants, the nearest and the second nearest neighbor approximation is usually made for quantitative analysis. For example, in the analysis of the HDS from the Jahn-Teller(JT) distortions in the colossal magnetoresistive(CMR) manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ [36], Campbell *et al.* took only the nearest neighbors into consideration, which are the oxygen atoms at the six corners of the MnO_6 octahedra. In this dissertation, we will follow the more general method developed by P.H.Dederichs[34] and W.A.Krivoglaz[35] where the concept of average “dipole force tensor” is introduced to take care of the total effect rather than considering the individual Kanzaki force $\vec{F}_{lk}$ exerted on the specific k -th

atom in the l -th unit cell.

With the acoustic approximation, we still need to know the $\vec{e}_k(\vec{q}j)$ and $\omega_{\vec{q}j}$ of the acoustic phonon modes to evaluate Eqn.(3.22). It is known that the acoustic phonon modes at small q region can be well approximated with continuum elastic theory, which is theoretically much simpler than considering the atomic interaction at microscopic scale with the atomic force constant $\Phi_{\alpha\beta}^{lkl'k'}$. Next, we will translate Eqn.(3.22) into elastic continuum description.

Within elastic continuum theory, the lattice vibration can be written as[37],

$$\rho \ddot{u}_\alpha(\vec{R}) = \sum_{\beta\gamma\lambda} c_{\alpha\gamma\beta\lambda} \frac{\partial^2 u_\beta}{\partial R_\gamma \partial R_\lambda} \quad (3.23)$$

where ρ is the mass density of the material and $c_{\alpha\gamma\beta\lambda}$ are the macroscopic elastic constants.

Again, we can choose the solution to the above equation to have the wavelike character,

$$u_\alpha = v_\alpha e^{-i\omega t + i\vec{q} \cdot \vec{R}} \quad (3.24)$$

Substituting this solution into Eqn.(3.23), we find that,

$$\omega^2 v_\alpha = \sum_{\beta} \mathbb{D}_{\alpha\beta} v_\beta \quad \text{with} \quad \mathbb{D}_{\alpha\beta} = \left(\sum_{\gamma\lambda} \frac{c_{\alpha\gamma\beta\lambda}}{\rho} q_\gamma q_\lambda \right) \quad (3.25)$$

where $\mathbb{D}_{\alpha\beta}$ is called elastic dynamical matrix. The solutions to Eqn.(3.25) are the three acoustic phonon branches with elastic continuum approximation. The eigenvectors and eigenvalues will be denoted as $\vec{v}(\vec{q}j)$ and $\omega'_{\vec{q}j}$, respectively. From Eqn.(3.25), we can see that when $\vec{q} \rightarrow 0$, the right hand side vanishes. Thus, $\omega'(\vec{q} \rightarrow 0)$ should also vanish for the

non-trivial solution $\vec{v} \neq 0$. The microscopic theory of lattice dynamics should give exactly the same solutions as macroscopic elastic theory for the acoustic phonon modes at the long wave limit where $\vec{q} \rightarrow 0$. Applying the long wave limit to Eqn.(3.11), we have,

$$M_k \omega_{0j}^2 \frac{e_{k\alpha}(0j)}{\sqrt{M_k}} = \sum_{l'k'\beta} \Phi_{\alpha\beta}^{lk'l'k'} \frac{e_{k'\beta}(0j)}{\sqrt{M_{k'}}} \quad (3.26)$$

With the condition,

$$\frac{e_{k\alpha}(0j)}{\sqrt{M_k}} = \frac{e_{k'\alpha}(0j)}{\sqrt{M_{k'}}} \quad (3.27)$$

and Eqn.(3.6), the right hand side is zero and we have vanishing ω_{0j} when $\vec{q} \rightarrow 0$. The above condition means $e_{k\alpha}(0j)/\sqrt{M_k}$ does not depend on k and all the atoms within an unit cell move together and it is actually the solution of the acoustic modes at long wave limit[27].

Comparing Eqn.(3.8) with Eqn.(3.24) and Eqn.(3.26) with Eqn.(3.25), we have the relation,

$$v_\alpha(0j) = \frac{e_{k\alpha}(0j)}{\sqrt{M_k}} \quad (3.28)$$

This relation is exactly true at the long wave limit with $\vec{q} \rightarrow 0$ and reasonably hold up to certain $|\vec{q}|$ value. In the following discussion, we will apply this long wave approximation and substitute $e_{k\alpha}(\vec{q}j)/\sqrt{M_k}$ and $\omega_{\vec{q}j}$ with $v_\alpha(\vec{q}j)$ and $\omega'_{\vec{q}j}$. Thus, Eqn.(3.22) is transformed as,

$$I_{HDS} = |i \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \left(\sum_j \frac{v_\alpha(\vec{q}j) v_\beta^*(\vec{q}j)}{\omega_{\vec{q}j}^{'2}} \right) \sum_{l'k'\beta} F_{l'k'\beta} e^{-i\vec{q} \cdot \vec{R}_{l'k'}}|^2 \quad (3.29)$$

The summation over the acoustic phonon mode j can be further simplified using the orthonormality property of $v_\alpha(\vec{q}j)$. Eqn.(3.25) defines $v_\alpha(\vec{q}j)$ to within a normaliza-

tion constant. Substitute the relation between $v_\alpha(\vec{q}j)$ and $e_{k\alpha}(\vec{q}j)$ into the orthonormality conditions(Eqn.(3.12)), the constant can be found as,

$$\sum_{\alpha} v_{\alpha}^*(\vec{q}j)v_{\alpha}(\vec{q}j') = \frac{1}{M}\delta_{jj'} \quad \text{and} \quad \sum_j v_{\beta}^*(\vec{q}j)v_{\alpha}(\vec{q}j) = \frac{1}{M}\delta_{\alpha\beta} \quad (3.30)$$

Thus, the matrix of the eigenvectors $v_{\alpha}(\vec{q}j)$ is unitary with a factor $1/\sqrt{M}$. From Eqn.(3.25), we have the relation in the matrix form as,

$$\mathbb{D} \begin{bmatrix} v_1(\vec{q}, 1) & v_1(\vec{q}, 2) & v_1(\vec{q}, 3) \\ v_2(\vec{q}, 1) & v_2(\vec{q}, 2) & v_2(\vec{q}, 3) \\ v_3(\vec{q}, 1) & v_3(\vec{q}, 2) & v_3(\vec{q}, 3) \end{bmatrix} = \begin{bmatrix} v_1(\vec{q}, 1) & v_1(\vec{q}, 2) & v_1(\vec{q}, 3) \\ v_2(\vec{q}, 1) & v_2(\vec{q}, 2) & v_2(\vec{q}, 3) \\ v_3(\vec{q}, 1) & v_3(\vec{q}, 2) & v_3(\vec{q}, 3) \end{bmatrix} \begin{bmatrix} \omega'_{q1}{}^2 & 0 & 0 \\ 0 & \omega'_{q2}{}^2 & 0 \\ 0 & 0 & \omega'_{q3}{}^2 \end{bmatrix} \quad (3.31)$$

and the orthonormality and the closure properties in Eqn.(3.29) can also be written in the matrix form as,

$$\begin{bmatrix} v_1^*(\vec{q}, 1) & v_2^*(\vec{q}, 1) & v_3^*(\vec{q}, 1) \\ v_1^*(\vec{q}, 2) & v_2^*(\vec{q}, 2) & v_3^*(\vec{q}, 2) \\ v_1^*(\vec{q}, 3) & v_2^*(\vec{q}, 3) & v_3^*(\vec{q}, 3) \end{bmatrix} \begin{bmatrix} v_1(\vec{q}, 1) & v_1(\vec{q}, 2) & v_1(\vec{q}, 3) \\ v_2(\vec{q}, 1) & v_2(\vec{q}, 2) & v_2(\vec{q}, 3) \\ v_3(\vec{q}, 1) & v_3(\vec{q}, 2) & v_3(\vec{q}, 3) \end{bmatrix} = \frac{1}{M} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3.32)$$

and

$$\begin{bmatrix} v_1(\vec{q}, 1) & v_1(\vec{q}, 2) & v_1(\vec{q}, 3) \\ v_2(\vec{q}, 1) & v_2(\vec{q}, 2) & v_2(\vec{q}, 3) \\ v_3(\vec{q}, 1) & v_3(\vec{q}, 2) & v_3(\vec{q}, 3) \end{bmatrix} \begin{bmatrix} v_1^*(\vec{q}, 1) & v_2^*(\vec{q}, 1) & v_3^*(\vec{q}, 1) \\ v_1^*(\vec{q}, 2) & v_2^*(\vec{q}, 2) & v_3^*(\vec{q}, 2) \\ v_1^*(\vec{q}, 3) & v_2^*(\vec{q}, 3) & v_3^*(\vec{q}, 3) \end{bmatrix} = \frac{1}{M} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3.33)$$

Using above relations, we can easily get,

$$\frac{1}{M}\mathbb{D}^{-1} = \begin{bmatrix} v_1(\vec{q}, 1) & v_1(\vec{q}, 2) & v_1(\vec{q}, 3) \\ v_2(\vec{q}, 1) & v_2(\vec{q}, 2) & v_2(\vec{q}, 3) \\ v_3(\vec{q}, 1) & v_3(\vec{q}, 2) & v_3(\vec{q}, 3) \end{bmatrix} \begin{bmatrix} \frac{1}{\omega_{\vec{q}1}'} & 0 & 0 \\ 0 & \frac{1}{\omega_{\vec{q}2}'} & 0 \\ 0 & 0 & \frac{1}{\omega_{\vec{q}3}'} \end{bmatrix} \begin{bmatrix} v_1^*(\vec{q}, 1) & v_2^*(\vec{q}, 1) & v_3^*(\vec{q}, 1) \\ v_1^*(\vec{q}, 2) & v_2^*(\vec{q}, 2) & v_3^*(\vec{q}, 2) \\ v_1^*(\vec{q}, 3) & v_2^*(\vec{q}, 3) & v_3^*(\vec{q}, 3) \end{bmatrix} \quad (3.34)$$

whose right hand side is exactly the summation over the acoustic mode j , $\sum_j \frac{v_\alpha(\vec{q}j)v_\beta^*(\vec{q}j)}{\omega_{\vec{q}j}^2}$, in Eqn.(3.29). Thus, the I_{HDS} can be further simplified as,

$$I_{HDS} = \left| \frac{i}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G}\cdot\vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{l'k'} F_{l'k'\beta} e^{-i\vec{q}\cdot\vec{R}_{l'k'}} \right|^2 \quad (3.35)$$

Next, we will consider the summation of the Kanzaki forces with the phase factor $e^{-i\vec{q}\cdot\vec{R}_{l'k'}}$ where $\vec{R}_{l'k'}$ is the position of the k' -th atom in the l' -th unit cell. In the systems of our interest in this dissertation, the cuprates, the Kanzaki forces are mainly from the electrostatic Coulomb interactions between atoms. For the nearest neighbors of the defect, the size misfit of the defect might introduce extra repulsive forces due to the fact that each atom resists overlap with the electron distributions of neighboring atoms. The Coulomb force is generally of $1/R^2$ without considering the screening of the mobile electrons. In the lattice distortion case, further screening effect to the atoms a little bit away from the defects comes from the displacements of the near neighbor atoms. The screening effect will make the Coulomb force decrease even faster as a function of distance. Thus, it is reasonable to consider the summation of the Kanzaki forces only with an unit cell, which is already beyond the nearest and the second nearest neighbor approximation for the cuprates which usually have big unit cells with large number of atoms in them. With this approximation,

$\vec{q} \cdot \vec{R}_{l'k'}$ is a small quantity at small q region and we can expand the phase factor to the first order.

$$I_{HDS} = \left| \frac{i}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{l'k'} F_{l'k'\beta} (1 - i\vec{q} \cdot \vec{R}_{l'k'}) \right|^2 \quad (3.36)$$

It is not difficult to find out that $\sum_{l'k'} F_{l'k'\beta}$ equals zero. The counterforces exerted by the surrounding ions to the defect have the same magnitude as the Kanzaki force but with a negative sign. The summation of the counterforces should be zero since the defect is at equilibrium. Thus $\sum_{l'k'} F_{l'k'\beta}$ must also be zero. Then the above equation can be rewritten as,

$$I_{HDS} = \left| \frac{1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} \left(\sum_{l'k'} F_{l'k'\beta} R_{l'k'\gamma} \right) q_\gamma \right|^2 \quad (3.37)$$

The summation of the Kanzaki force dipole, $\sum_{l'k'} F_{l'k'\beta} R_{l'k'\gamma}$, ends up to be a three by three matrix, which will be denoted as $P_{\beta\gamma}$ and is called the dipole force tensor. With the P matrix, the I_{HDS} can be written in a simpler form as,

$$I_{HDS} = \left| \frac{1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} P_{\beta\gamma} q_\gamma \right|^2 \quad (3.38)$$

In the above discussion, the vector $\vec{q}$ satisfies the relation $\vec{Q} + \vec{q} = \vec{G}$. Conventionally, we prefer to use $\vec{q}$ to denote the vector of the wavevector transfer $\vec{Q}$ relative to Bragg peak $\vec{G}$ in X-ray scattering, which is $\vec{Q} - \vec{G}$. Thus, a minus sign is added to above equation and it becomes,

$$I_{HDS} = \left| \frac{-1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} P_{\beta\gamma} q_\gamma \right|^2 \quad (3.39)$$

This minus sign is important when the scattering from the strain fields interferes with the scattering from other sources. In the following discussion, it will be omitted if only the HDS

is considered.

Now we can see the advantage of translating the problem of X-ray diffuse scattering from lattice distortion due to the defects into the elastic continuum theory language. The material properties involved in this problem are condensed into the $\mathbb{D}^{-1}$ matrix. Also, the Kanzaki forces exerted on individual atoms will be summed up to give an average effect. Even though by doing the summation over all the atoms we lose the detailed local informations, the amount of parameters involved in I_{HDS} calculation is dramatically reduced. More importantly, from the fitting point of view, the possibility of reducing fitting parameters suggests that the original set of parameters are highly entangled with each other and the fitting result will be of high uncertainties. In another words, the X-ray diffuse scattering technique will only give us certain amount of informations about the dopant introduced lattice distortion rather than the full details of the Kanzaki forces exerted on individual atoms. This is the limitation of the HDS analysis, especially in the case of studying the materials constructed by non primitive unit cells which contain large number of atoms. But, in most cases, it is the long range strain introduced by the defects that affect the macroscopic properties the most, such as thermal transport, conductivity *etc.* rather than the unit cells containing the defects. The HDS analysis is fully capable of revealing the formation of the long range strain which is typically of nano meter scale, as will be demonstrated later in this thesis. The very local atomic displacements within the unit cell containing the defect can be studied with other techniques, such as the Extended X-Ray Absorption Fine Structure(EXAFS). EXAFS can give information about the bond-length change of specific atom pairs within the unit cell due to the defects. Thus, combining HDS and EXAFS together, a full picture of the defect introduced lattice distortion can be achieved, from sub-angstrom

to nano-meter scale.

3.3.5 Multiple defect centers

Huang diffuse scattering from single defect was discussed in previous section. But, for a real material which is doped to achieve certain kinds of functions, the amount of dopants need to reach a certain level to alter the electronic or structural properties of the parent compound macroscopically. For example, there is threshold for the percentage of dopants, above which the high temperature superconductivity can be realized. In this sense, we are always dealing with multiple defects in real materials. The distribution of the dopants and their effect on the local structure can be very complicated. Here we restrict our discussion with the assumptions that:

- the dopants do not change the local elastic properties significantly and the unit cells close to the dopants mediate the elastic strain in the same way as the average lattice does.
- the dopant introduced lattice distortions are small. The overall lattice distortions can be regarded as linear superposition the the lattice distortions introduced by individual defect centers.

With the assumptions listed above, Eqn.(3.39) can be modified for multiple defects case as,

$$I_{HDS} = \left| \frac{\sum_t c_t e^{i\vec{Q} \cdot \vec{R}_t}}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} P_{\beta\gamma} q_\gamma \right|^2 \quad (3.40)$$

where c_t is the defect occupation function in the t -th unit cell. It is 1 when there is a defect and 0 when there is no defect in the unit cell t . $\vec{R}_t$ is the displacement vector for the t -th

unit cell accordingly. With the relation, $e^{i\vec{R}_t \cdot \vec{G}} = 1$, the above equation can be simplified as,

$$I_{HDS} = \left| \frac{1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} P_{\beta\gamma} q_\gamma \right|^2 \left| \sum_t c_t e^{i\vec{q} \cdot \vec{R}_t} \right|^2 \quad (3.41)$$

In the simple case, the modulus square of the Fourier transform of the defect distribution function c_t serves as an envelope to the Huang diffuse scattering from a single defect. Even though the equation looks simple, it is impossible to know the exact distribution of the defects in most cases. c_t not only depends on the properties of the defects, but also depends on the sample growing conditions, annealing procedures, *etc.* Here we briefly discuss two extreme cases: the dopants are well ordered to form “super dopant lattice”; or the dopants are totally randomly distributed.

If the dopants are well ordered and c_t is a periodic function of position, the factor $|\sum_t c_t e^{i\vec{q} \cdot \vec{R}_t}|^2$ gives superstructure peaks, Analogous to the discussion given in Section 3.2. Thus the HDS will be strongly modified comparing with that of single defect scenario.

Next, we discuss the statistical average of $|\sum_t c_t e^{i\vec{q} \cdot \vec{R}_t}|^2$ assuming the dopants are totally randomly distributed. Assuming $\langle c_t \rangle = c$, we have,

$$\langle \left| \sum_t c_t e^{i\vec{q} \cdot \vec{R}_t} \right|^2 \rangle = \langle \left| \sum_t (c_t - c) e^{i\vec{q} \cdot \vec{R}_t} + c \sum_t e^{i\vec{q} \cdot \vec{R}_t} \right|^2 \rangle \quad (3.42)$$

From previous discussion, we know that $\sum_t e^{i\vec{q} \cdot \vec{R}_t} = 0$ when $\vec{q} \neq \vec{G}$. This is satisfied from the definition of $\vec{q}$. Thus the second term vanishes and Eqn.(3.42) gives,

$$\langle \left| \sum_t c_t e^{i\vec{q} \cdot \vec{R}_t} \right|^2 \rangle = \langle \sum_t (c_t - c)^2 \rangle + \langle \sum_{t \neq t'} (c_t - c)(c_{t'} - c) e^{i\vec{q} \cdot (\vec{R}_t - \vec{R}_{t'})} \rangle \quad (3.43)$$

Assuming the dopants are randomly distributed, the correlation of the dopant position can be ignored so that the second term equals zero. Since c_t can have only the values 0 and 1, $\langle c_t^2 \rangle = \langle c_t \rangle = c$. Then the statistical average becomes,

$$\langle |\sum_t c_t e^{i\vec{q} \cdot \vec{R}_t}|^2 \rangle = Nc(1 - c) \quad (3.44)$$

where N is the total number of unit cells. Now we can see that, by assuming the dopants are randomly distributed, the HDS pattern is the same as that due to single defect. Only the intensity is scaled up by a constant factor $Nc(1 - c)$.

$$I_{HDS} = Nc(1 - c) \left| \frac{1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_\beta \mathbb{D}_{\alpha\beta}^{-1} \sum_\gamma P_{\beta\gamma} q_\gamma \right|^2 \quad (3.45)$$

A random distribution of the dopants are most likely to be realized in samples with low dopant concentration. When the dopant concentration is low and the distance between the dopants is large, we can assume no overlapping of the strongly distorted regions around individual dopants. Thus the individual dopants will be regarded to be independent to each other and the correlation between dopants positions often can be ignored. Another merit of low dopant concentration for HDS analysis is that the chance of dopants clustering, which might affect the local elastic properties significantly, is lowered. This helps to justify the first assumption we made at the beginning of this section.

The samples for our experiments were carefully chosen for HDS studies. For the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ family, the experiments carried out on samples with x to be 0.08, which are underdoped but have superconducting transition temperature ($\sim 20K$) well separated from the lowest temperature ($\sim 7K$) reachable with the instruments. For the $\text{YBaCu}_2\text{O}_{7-x}$, x

is chosen to be 0.08. For HDS study alone, it is preferable to have x even smaller. But the lower limit of x under 1 atm of O_2 appears to be about 0.04[38]. Thus, crystals with smaller x will be unstable in air. Also, other interesting phenomena, such as oxygen vacancy ordering, was observed at this composition, which will be discussed later.

X-ray Diffuse Scattering from under doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The cuprat $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was among the first high-temperature superconductors discovered and has been extensively studied by various techniques. It is believed to have the simplest structure among all cuprate families in which the individual CuO_2 planes are separated from each other by the charge reservoir layers, unlike, for example the $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ family which has three adjacent CuO_2 planes. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, every Cu atom is at the center of an oxygen octahedron as shown in Fig.(4.1). Upon doping, the La^{3+} are randomly replaced by Sr^{2+} , and thus fewer electrons are donated to the CuO_2 planes. In another words, holes are created and they are believed to mainly reside in the CuO_2 planes. As a function of doping and temperature, phase transitions occur in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, both electronically and structurally(Fig.(4.1)). At high temperature, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystal structure is tetragonal which is called the high temperature tetragonal(HTT) phase. Below the structural phase transition temperature, the CuO_6 octahedral

starts to rotate about the tetragonal $(1\ 1\ 0)$ axis and the crystal structure becomes orthorhombic(Fig.(4.2)), which is called the low temperature orthorhombic(LTO) phase. The axis of the rotation is defined as the **a**-direction in the LTO phase. In this dissertation, the orthorhombic crystal structure notation will be used unless specified otherwise. The structural phase transition temperature decreases as the doping rate increases and disappears at a Sr concentration of $x \sim 0.2$. The superconductivity appears for Sr concentration $0.05 < x < 0.32$ and the highest transition temperature($T_c \sim 40K$) is achieved with $x \sim 0.15$.

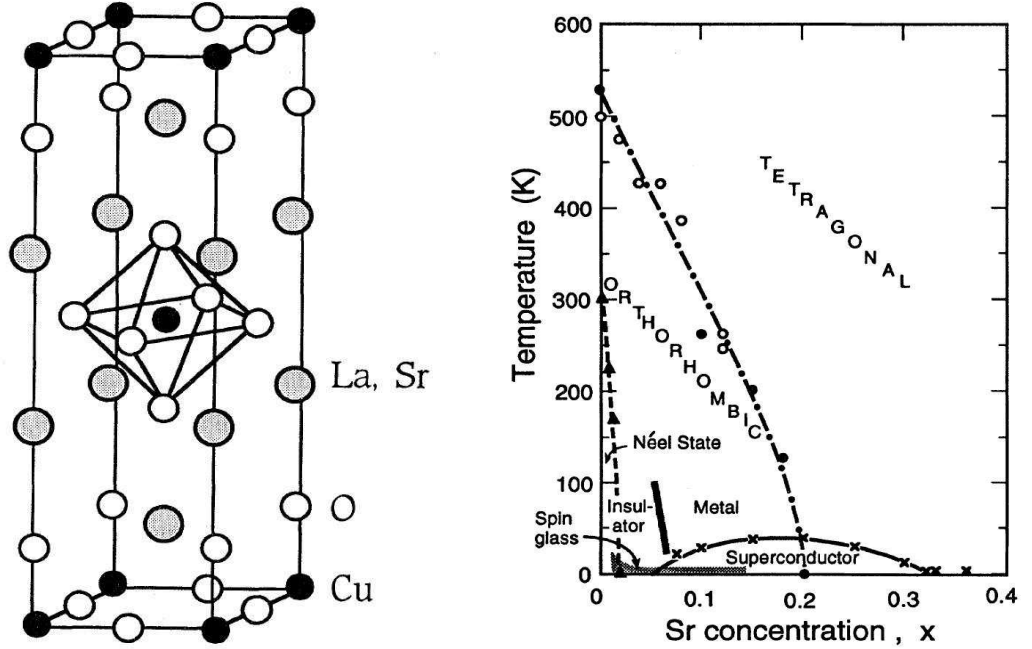


Figure 4.1 Left: crystal structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in high temperature tetragonal phase. Taken from Almasan and Maple(1991)[1]. Right: phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Taken from Keimer *et al.*(1992)[2]

Since the Sr^{2+} are less positively charged than the La^{3+} they substitute, they inevitably perturb the local electronic structure. On the other hand, the Coulomb forces

exerted by the Sr^{2+} on the surrounding ions are different from those exerted by the La^{3+} . These Kanzaki forces due to static electronic interactions, introduced in the previous chapter, need to be balanced by local lattice distortion. Also, the ionic radius of Sr^{2+} is larger than that of the La^{3+} . The repulsive forces to the nearest neighbors, which is due to the fact that each ion resists overlap with the electron distributions of neighboring ions, is larger for the Sr^{2+} . These are also Kanzaki forces of another kind and they will further distort the local lattice structure. Thus, the Sr^{2+} perturbs the local properties and introduce disorder into the system, both electronically and structurally. Since the high temperature superconductivity is realized by off-stoichiometric doping, dopant-introduced local disorder generally exist in all cuprates. The disorder associated with the dopants have been natu-

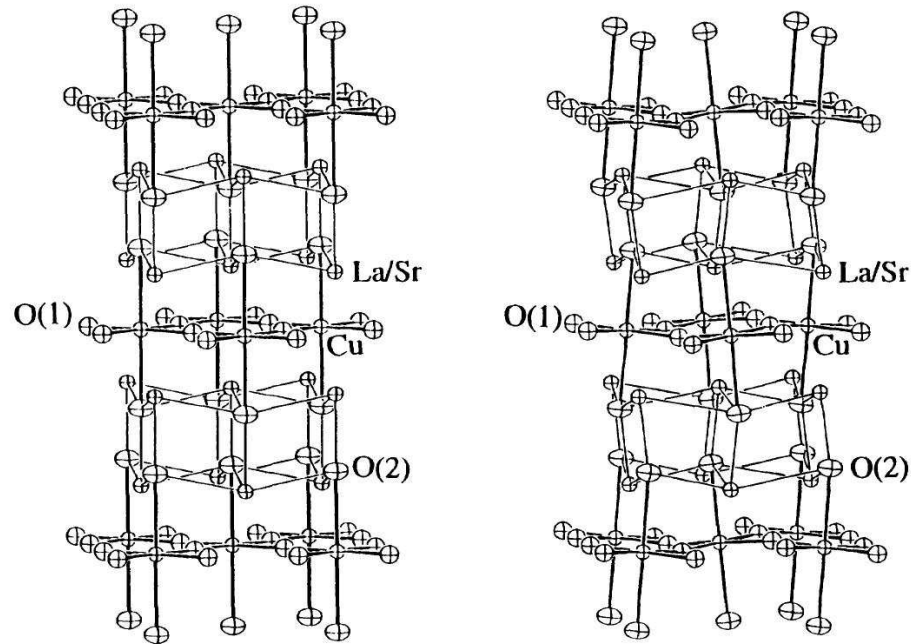


Figure 4.2 Sketch of the HTT(left) to LTO(right) structure phase transition by the rotation of the CuO_2 octahedral. The orthorhombic **a** axis is perpendicular to the plane of the paper and the **b** axis is horizontal. From P.G.Radaelli *et al.*[3]

rally identified as the origin of the remarkable electronic inhomogeneities recently revealed by scanning tunneling microscopy (STM) studies [14, 15, 16, 39] where nano-scale variations of the pairing gap width and local density of states (LDOS) have been observed in many different cuprate families.

If the observed electronic inhomogeneities are due to dopants, a better understanding of the local lattice distortion and strain associated with the dopants is crucial to address the interplay of the dopant-induced disorders and the superconductivity in cuprates. Indeed, the effect of the strain in cuprates on superconductivity has long been noticed by hydrostatic experiments [40, 41] where T_c can be tuned by pressure of the order of 0.1 K/GPa. More dramatic effects were seen in uniaxial pressure experiments [42, 40, 43] where the effect of pressure on T_c can be an order higher and shows strong anisotropic behavior. Thus, together with the STM observations, a detailed study of the internal lattice distortion and strain associated with the dopants may help us understand to what extent structural inhomogeneity influences electronic inhomogeneities in cuprates. In this chapter, we will discuss our X-ray diffuse scattering experiments on underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, in which the nano-scale electronic inhomogeneities were also observed [39].

Another possible source which could introduce local lattice disorder in cuprates is the long suspected “polaron”. When the electron-phonon coupling is strong and the kinetic energy of the charged carriers is not high enough, the carriers may be self-trapped by inducing structural distortion to their surrounding lattice [44]. Polaron-related models have been discussed by many theoretical works to explain the high temperature superconductivity phenomena [45, 46, 47, 48]. Experimentally, the formation of polarons in cuprates has been suggested by optical conductivity measurements [49, 50] and angle-resolved photoemission

spectroscopy measurements[51, 52, 53]. A polaron consists of a localized charge with its associated lattice distortion field, which will also give rise to diffuse scattering around the Bragg peaks. W. Dmowski *et al.* have related their X-ray diffuse scattering experimental results on LSCO to the formation of polarons[54]. We will comment on this in our discussion.

4.1 Sample preparation

X-ray diffuse scattering from the lattice distortion due to a single defect was discussed in the previous chapter. When the defect concentration is low, they can be regarded as randomly distributed and far away from each other. Thus we can ignore the correlation between defect positions and assume the scattering from individual defect centers can be added up incoherently. If the defect concentration is high, other effects, such as clustering and interference between nearby defect centers, will complicate the X-ray diffuse scattering pattern and add difficulties to the quantitative analysis. Thus, we deliberately chose the underdoped $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ for our experiments, which has low Sr concentration but is still in the superconducting region as shown in Fig.(4.1).

A high quality single crystal of $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ was provided by Dr. S.Wakimoto at Japan Atomic Energy Agency. The crystal was grown by the travelling-solvent floating-zone technique. Dried powders of La_2O_3 , SrCO_3 , and CuO of 99.99% purity were used as starting materials for feed rods and solvents. The powders were ground and baked in air for 12 hours at 900°C followed by an additional grinding process. Feed rods were shaped under hydrostatic pressure and sintered in air at 900°C for 12 hours and at 1150°C for an additional 12 hours. 2 moles of excess CuO was added into the feed rods to compensate the

for the evaporation of CuO during the high temperature growth.

The original crystal was of cylindrical shape with a radius of $\sim 3mm$ and a height of $\sim 8mm$. Samples of slab shape with well defined orientation and certain dimensions are required for X-ray scattering experiments. Thus, small pieces with the dimension to be about $0.5 \times 2 \times 4$ mm were cut from the big crystal. The cutting was done with a wire saw(model 850 from South Bay Technology INC.). In order to minimize the damage to the sample surface during cutting, we chose the thinnest stainless steel wire available with the wire diameter to be 0.005". The abrasive slurry used was a mixture of Glycerol, water and B_4C fine powders(~ 10 microns in size). A backscattering Laue picture was taken and later on fitted with the software OrienExpress(V3.3) from J.Laugier to determine the orientation of the crystal. With the obtained orientation information, the crystal was carefully mounted onto the wire saw stage to ensure that the faces and edges of the final slabs corresponded to major crystal axis directions. Fig.(4.3) shows the Laue pattern taken after the cut perpendicular to the $(1\ 0\ 0)$ direction for one piece of our samples. The $[1\ 0\ 0]$ Bragg peak is almost at the center of the back scattered beam with the angular orientation error to be less than 1° . Samples with well defined orientations are advantageous for single crystal X-ray scattering experiments. They minimize the survey range in reciprocal space required to find certain Bragg peaks on a X-ray diffractometer with a point detector. The orientation and cutting work was done in Professor Maple's laboratory at UC San Diego.

After the samples were cut, they were polished to get rid of the first $\sim 100micron$ surface layers which might have been damaged during the cutting process. Also, a smooth surface is needed for X-ray scattering experiments to reduce the diffuse scattering from surface roughness. This is especially important for our X-ray diffuse scattering experiments

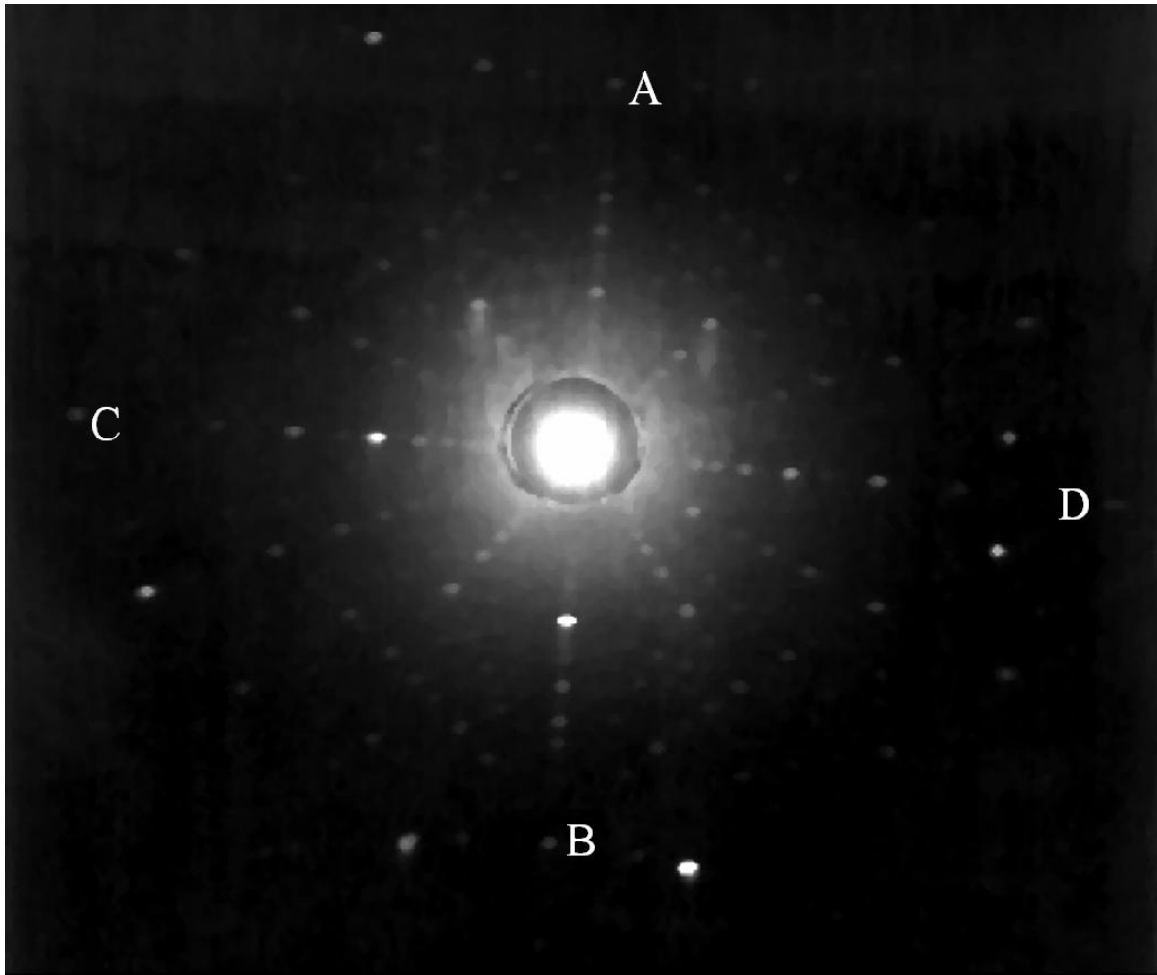


Figure 4.3 Backscattering Laue pattern from $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$. The Bragg peaks labeled as A, B, C and D are $[-1\ 0\ -1]$, $[-1\ 0\ 1]$, $[-2\ 1\ 0]$ and $[-2\ -1\ 0]$, respectively.

where the signals from the lattice distortions are expected to be very weak. The polishing was done with Dr. Jennifer Zheng's help at Material Science Division of Argonne National Laboratory using a lapping machine. The finest abrasive papers used were coated with Al_2O_3 with grain size to be less than 3 microns. The polishing was done in a very gentle way to get the best polished surfaces possible with the available instruments and it took 4 to 5 hours to finish one surface.

To further remove the stress formed during the cutting and polishing treatments, the samples were annealed with the help from D.Hinks at Material Science Division of

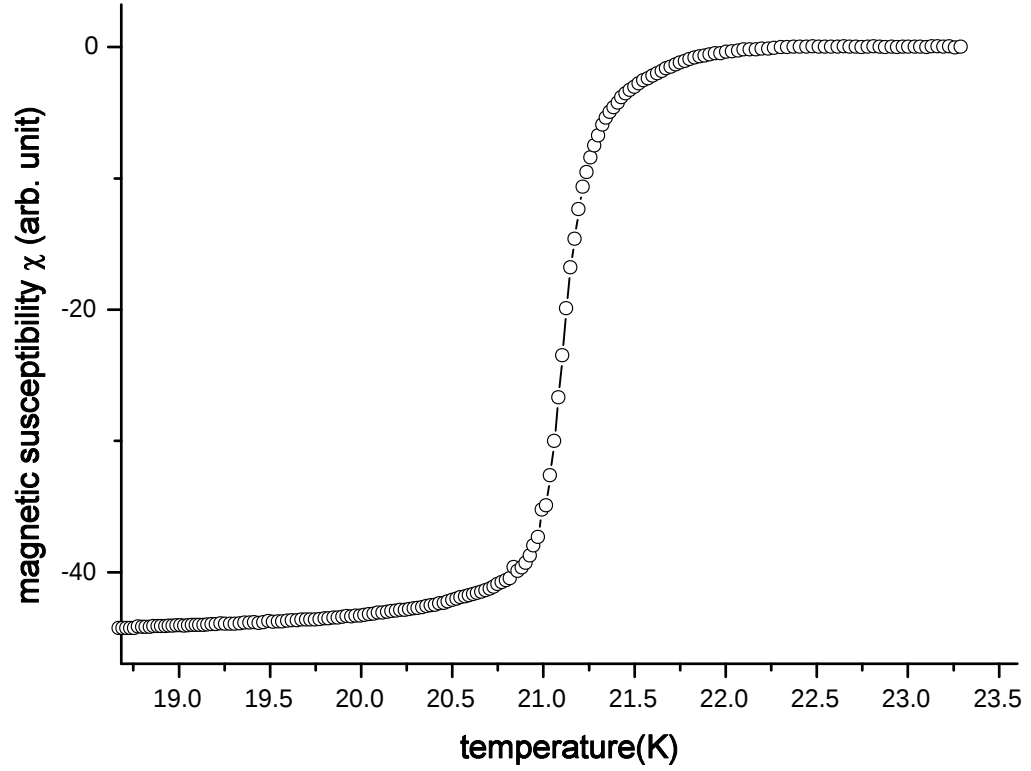


Figure 4.4 Magnetic susceptibility curve for one of the samples measured with SQUID with DC mode. The applied field is 0.1G.

Argonne National Laboratory. The annealing was done in oxygen flow with one atm pressure at 825°C for 24 hours and then 500°C for 20 hours. After the annealing, the magnetic susceptibility curves were measured with SQUID in DC mode by H.Claus at Material Science Division of Argonne National Laboratory. The samples were first cooled down to $\sim 4K$ with zero field. Then 0.1 Gauss field was applied to measure the magnetic susceptibility as a function of increasing temperature. Fig.(4.4) shows a typical magnetic susceptibility curve measured. The smoothness and sharpness($\Delta T \sim 1K$) of the superconducting transition edge indicate the high quality of our samples. The T_c is determined to be 21.1K from the middle point of the transition edge.

4.2 Experimental aspects

Our X-ray diffuse experiments on $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ were performed on the X-Ray Operations and Research 4-ID-D beam line at the Advanced Photon Source(APS) at the Argonne National Laboratory and the X-ray scattering experimental station 7-2 at the Stanford Synchrotron Radiation Laboratory. The very intense X-ray radiation with tunable energy makes the synchrotron light sources the ideal tool to study the weak diffuse scattering from small crystals. We will mostly focus on the data taken on the APS 4-ID-D beam line which provides higher energy X-rays and better resolution. From the batch of samples prepared, we chose the one which had the best polished surfaces with its largest surface to be an (0 0 1) surface. All the data was taken in reflection geometry.

Fig.(4.5) is the sketch of the 4ID beam line lay-out. The samples are mounted on a closed cycle cryostat and are sealed inside a Beryllium chamber. The whole system can be cooled down to $\sim 6K$.

The $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ crystal undergoes a HTT to LTO structural phase transition with the transition temperature to be $\sim 280K$ [55] and forms twinned domains at low temperature. With large beam beam size(0.5x0.5 mm), the two sets of Bragg peaks from two different domain configurations were clearly seen. Fig.(4.6) shows the two-dimensional scans around the (2 0 28) Bragg peak in the **a-b** plane. Except the center (2 0 28) Bragg peak, the other peak sitting at (1.98 0.02 28) was also observed, which is actually the (0 2 28) Bragg peak from the other twined domain and will be denoted as (0 2 28)'.

Typically, STM measurements are carried out on a single domain. In order to directly compare the X-ray diffuse scattering observations with STM results, ideally we want to scatter from a single domain grain to eliminate direction confusion about **a-b** axes

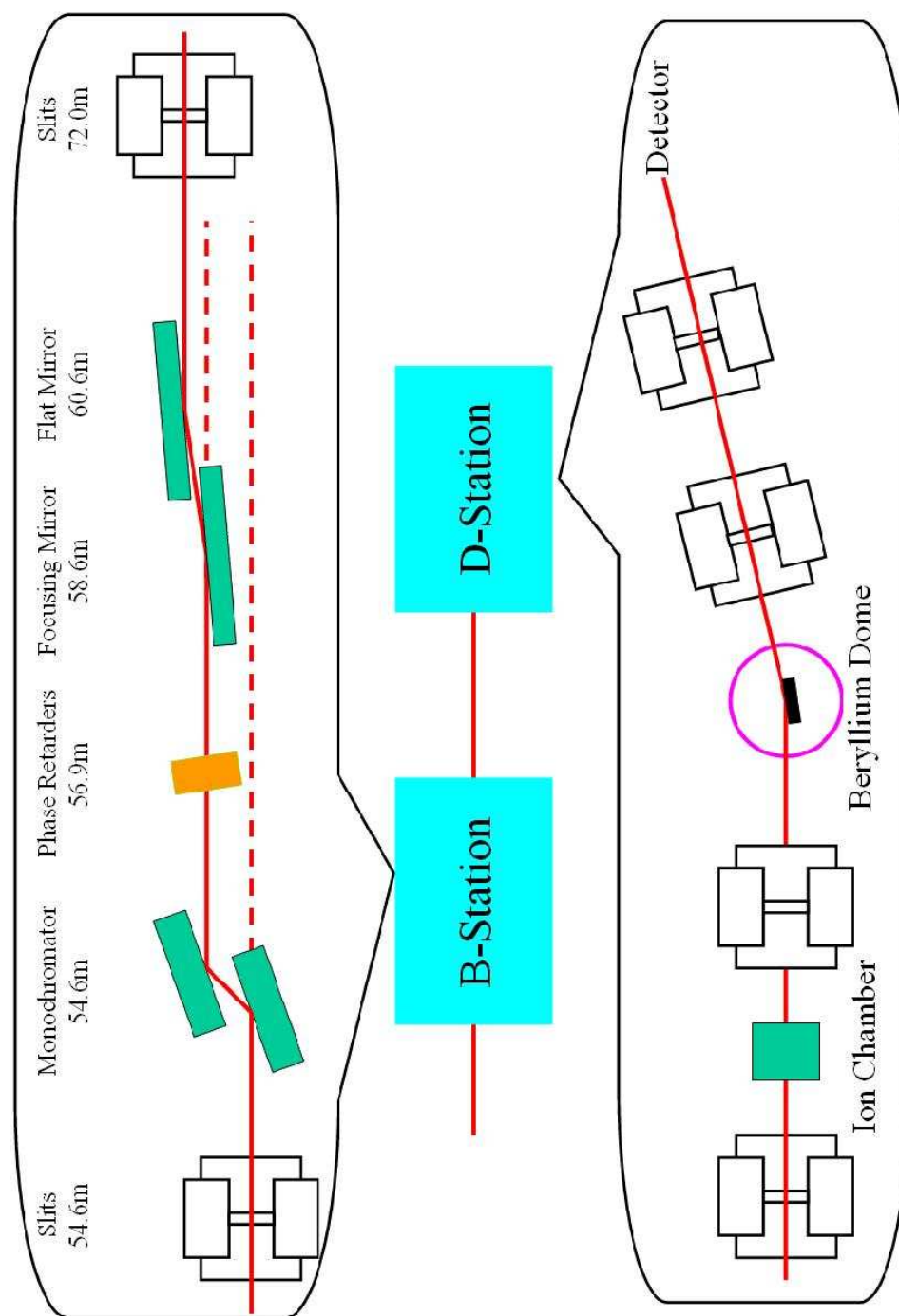


Figure 4.5 Sketch of the 4ID-B and 4ID-D stations at APS. Upper panel: optical components in the B-station. The distances are from the undulator. Bottom panel: experimental components in the D-station. The samples are sealed inside a Beryllium Dome.

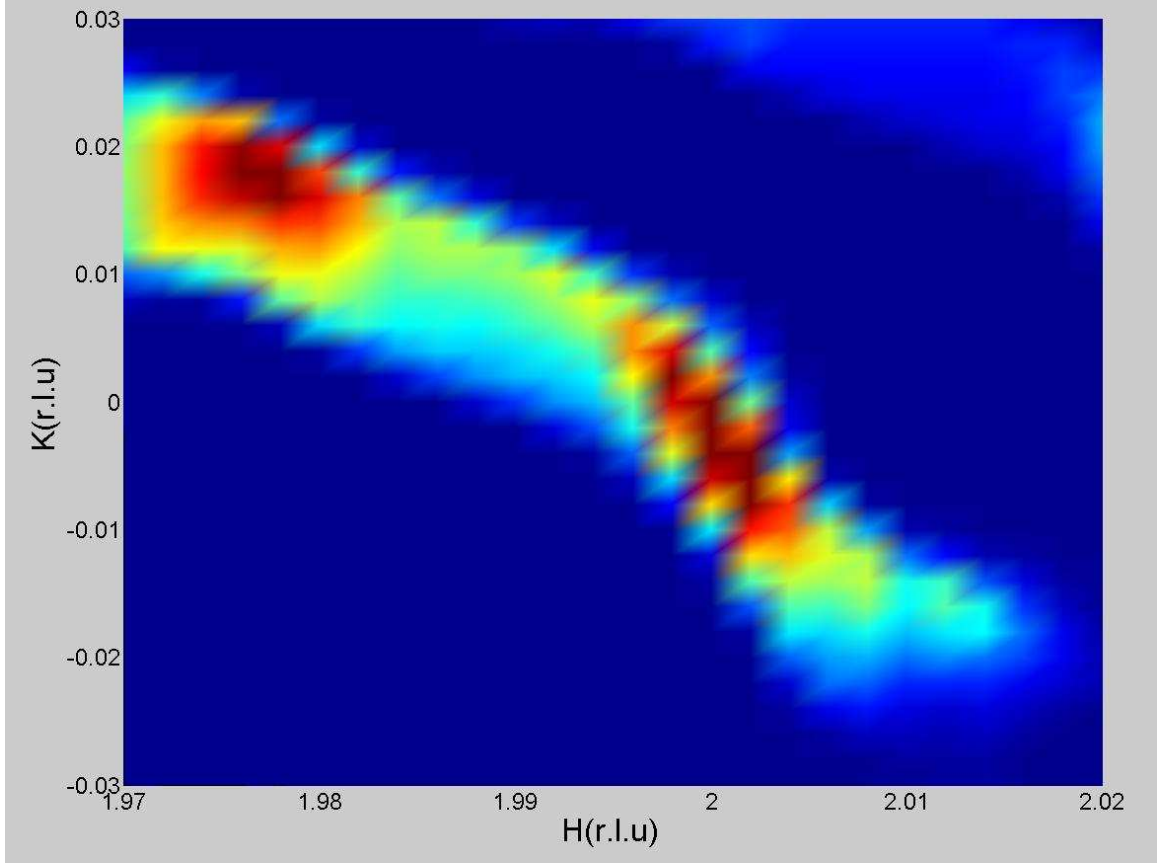


Figure 4.6 Two-dimensional scans around (2 0 28) Bragg peak, showing the twinning structure in the LTO phase.

and avoid the domain averaging effect. This was achieved by carefully tuning the beam size and selecting the scattering spot on the sample via sample spatial translation. By cutting down the beam size to 0.3 X 0.18 mm and translating the sample, we managed to minimize one set of the Bragg peaks until it was negligible comparing with the remaining set.

The relative volume ratio of the two sets of domains illuminated by the X-ray beam can be estimated by comparing the Bragg peak intensities of (2 0 22) with that of (0 0 22). The reason to choose L=22 will be explained in later discussion. Assuming the volume percentage of the two sets of domains are X and Y respectively, we have the relation

$X + Y = 1$ and,

$$X * \frac{\text{total Measured } (0\ 0\ 22) \text{ intensity}}{\text{Measured } (2\ 0\ 22) \text{ intensity}} = \frac{\text{calculated } (0\ 0\ 22) \text{ intensity of a single domain}}{\text{calculated } (2\ 0\ 22) \text{ intensity of a single domain}} \quad (4.1)$$

because the measured $(0\ 0\ 22)$ Bragg peak intensity get contributions from both sets and they just add up without interference. The measured ratio of the overall $(0\ 0\ 22)$ Bragg peak intensity to the $(2\ 0\ 22)$ Bragg peak intensity of the remaining set is 1.33 and the calculated ratio is 1.18. Thus, we can determine X to be 0.88, which means almost 90% of the sample volume illuminated by the X-ray beam is of one domain configuration. Later we will see that the ability to get scattering mostly from a single domain is crucial for our experiments which eliminated the domain averaging effect and revealed the strong anisotropy of strain associated with the dopants in the **a-b** plane.

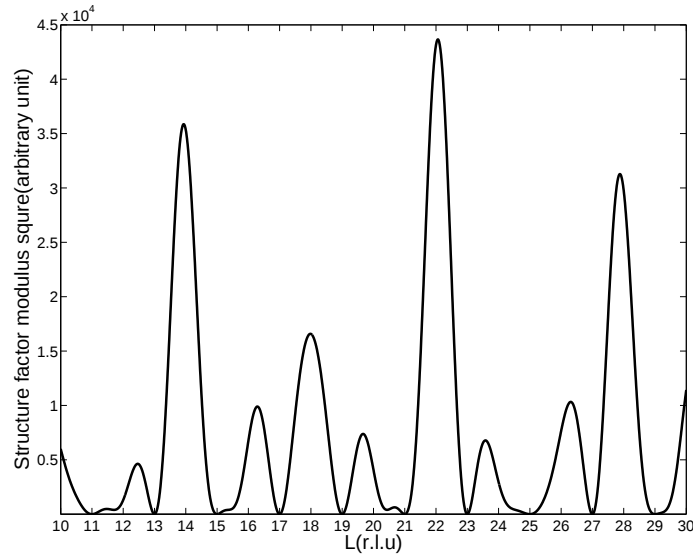


Figure 4.7 The square modulus of the structure factor as a function of L for $\vec{Q} = (00L)$.

As we have shown in the previous chapter in Eqn.(3.39), the intensity of HDS

is proportional to $|\sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k}|^2$, which is essentially the square modulus of the structure factor for the center Bragg peak. It is also proportional to $|\vec{Q}|^2$. Thus, in order to get strong HDS, it is favorable to perform our experiments around Bragg peaks with high Q value and large structure factor. In Fig.(4.7), we show the square modulus of the structure factor for $\vec{Q} = (0, 0, L)$ in a big L range.

From Fig.(4.7), we can see that the square modulus of the structure factor peaked at $L=22$. With the X-ray energy to be 19.924KeV used for our experiments, this large Q is reached by rotating the detector arm by ~ 60 degree in the vertical plane. In Fig.(4.8), we

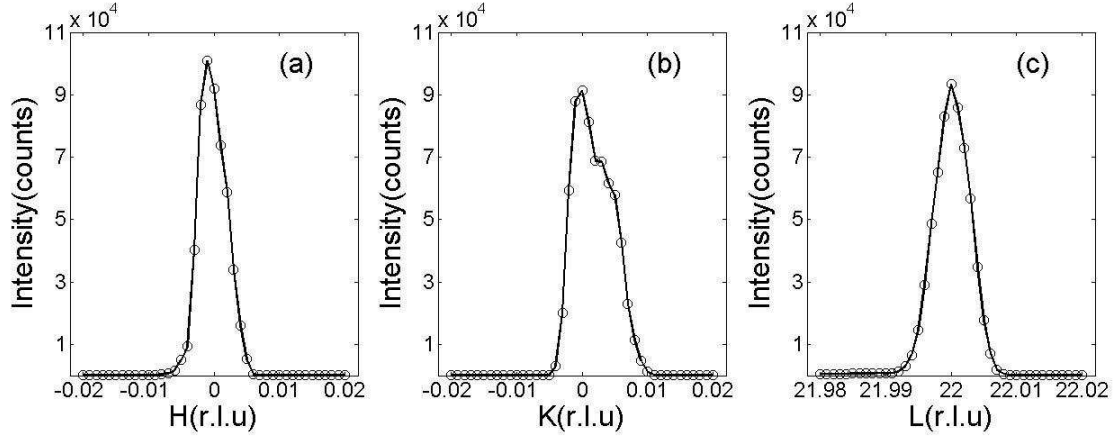


Figure 4.8 Line scans crossing the (0 0 22) Bragg peaks along the three major crystal direction.

show the scans crossing the (0, 0, 22) Bragg peak along the three major crystal directions. The $\mathbf{K}$ -direction scan has the biggest full width half maximum to be $0.008 \frac{2\pi}{b}$, indicating the mosaic spread of the sample to be less than 0.02° .

4.3 Diffuse scattering

Two dimensional X-ray diffuse scattering scans from $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ around $(0, 0, 22)$ and $(-2, 0, 22)$ Bragg peaks are shown in Fig.(4.9) in the upper panel. The data was collected at $\sim 7K$ to minimize the thermal diffuse scattering contribution. In the bottom panel, we show together the calculated Thermal Diffuse scattering pattern based on Eqn.(2.19).

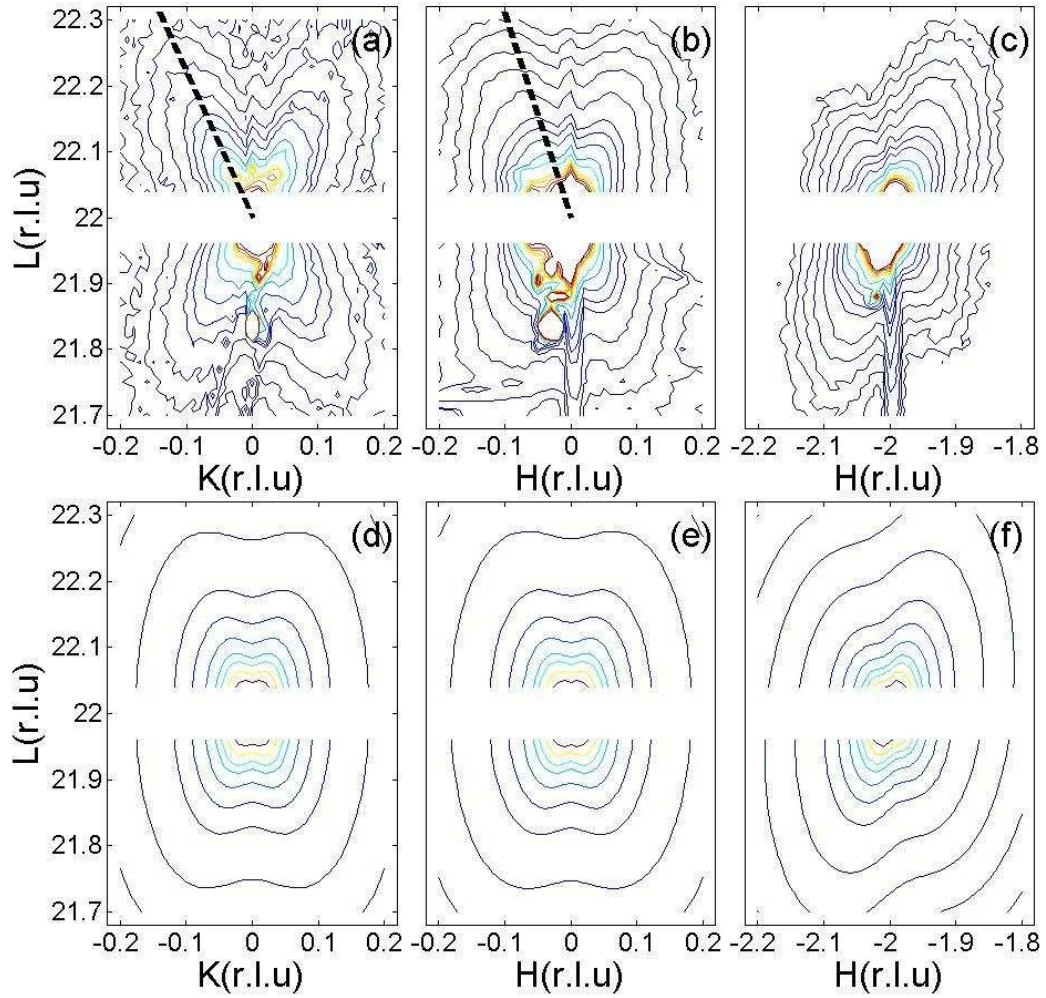


Figure 4.9 (a): 2-D mesh in the **K-L** plane around $(0\ 0\ 22)$. (b): 2-D mesh in the **H-L** plane around $(0\ 0\ 22)$. (c): 2-D mesh in the **H-L** plane around $(-2\ 0\ 22)$. (d), (e) and (f) are the calculated TDS accordingly.

Qualitative difference between the expected TDS and the experimental data is clearly seen. The observed diffuse scattering shows stronger anisotropy in the reciprocal space than the calculated TDS, indicating large portion of the observed diffuse scattering intensity is of other origin. To verify that the extra contribution are the HDS from the local lattice distortion, the q dependence of the diffuse scattering intensity was analyzed.

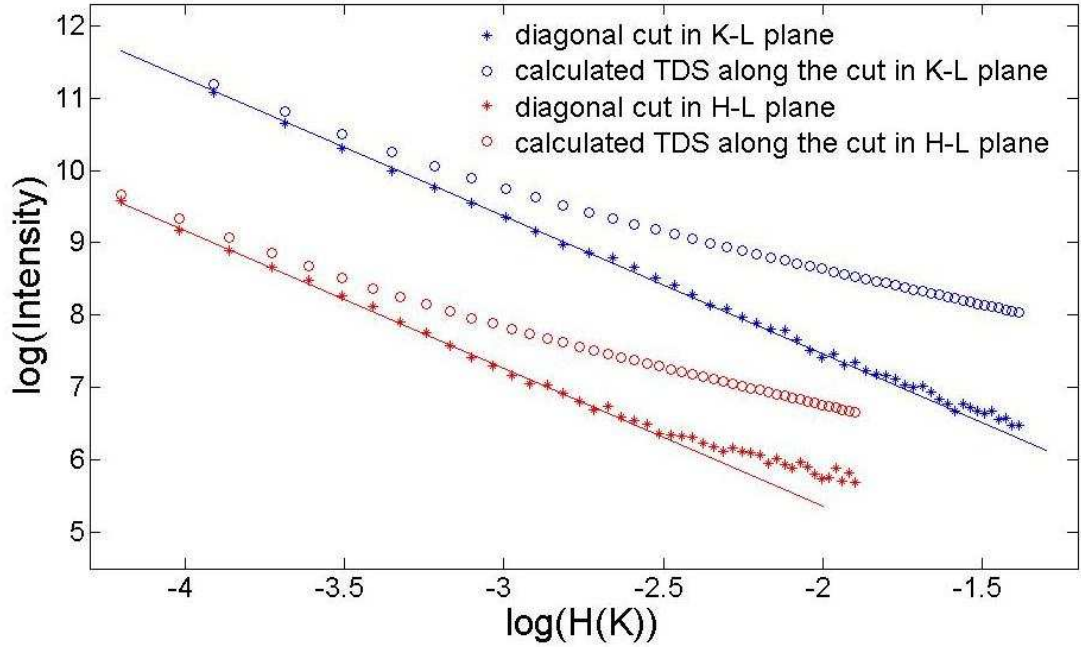


Figure 4.10 asterisk: Log-Log plot of the diagonal scans indicated in Fig.(4.10). Circle: calculated TDS accordingly. The slope for both blue and red lines is 1.9. The intensities for all the curves are scaled to be put into one plot.

The HDS has a general q dependence as $1/q^\nu$. Since the elastic dynamic matrix $\mathbb{D}_{\alpha\beta}$ is proportional to q^2 (Eqn.(3.25)), we have $\nu = 2$ for HDS from Eqn.(3.39). For the TDS, the intensity versus q relation is complicated because the thermal population factor, $\coth \frac{\hbar\omega_j(\vec{q})}{2KT}$, depends on temperature (Eqn.(2.20)). A general q dependence as $1/q^\nu$ with a constant ν is true only with special conditions. When the temperature is high

enough, at which $\frac{\hbar\omega(\vec{qj})}{2KT} \ll 1$, the thermal population factor is proportional to $1/\omega(\vec{qj})$ and we have $\nu = 2$. When the temperature is close to zero Kelvin, at which $\frac{\hbar\omega(\vec{qj})}{2KT} \gg 1$, the population factor is 1 without excitation and we have $\nu = 1$. When $T \sim 7K$, at which the

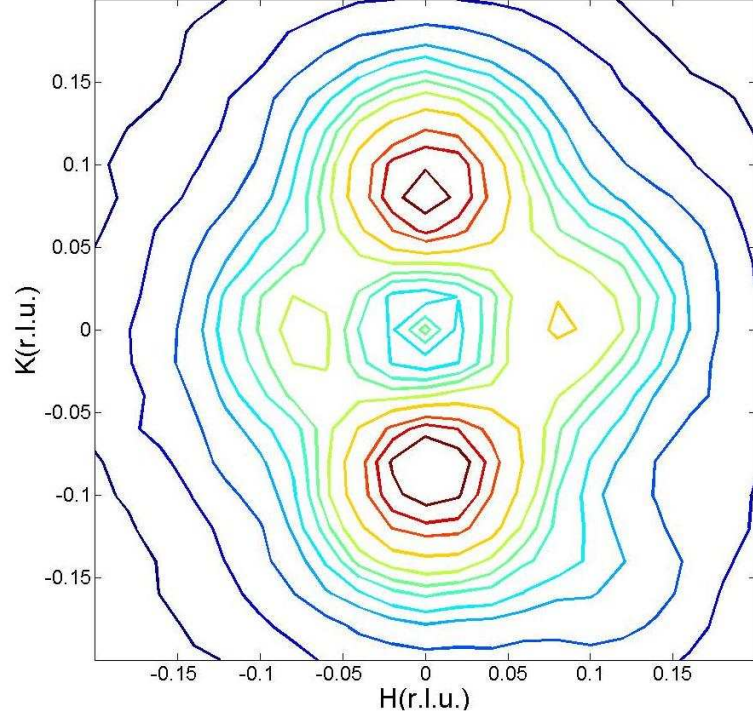


Figure 4.11 2-D mesh of the diffuse scattering in the H-K plane with $L=22.2$. The offset from (0 0 22) is to avoid the strong Bragg peak.

diffuse scattering data presented in Fig.(4.8) was collected, the TDS shows no general $1/q^\nu$ behavior. $\delta \log(TDS)/\delta \log(q)$ is less than 2 and approaches 1 when the phonon energy is much greater than KT ($KT \sim 0.6 meV$ for $7K$). This is demonstrated clearly in Fig.(4.10). The slope of the TDS log-log plot is less than 2 when q is close to zero and gradually becomes 1. This behavior is totally different from that of the observed data which shows $1/q^\nu$ dependence with $\nu = 1.9$ in a big q range, starting from $q \sim 0$. This unambiguously proves that the dominant contribution to the observed diffuse scattering is of HDS nature.

The small deviation of the ν from 2 is due to a certain amount of HDS and background, which vary slowly as a function of q .

Since the HDS decreases down much faster than TDS as a function of q , a cross-over from HDS to TDS is seen for the cut in H-L plane where the slope of the log-log plot turns towards 1 at higher q value. Interestingly, this cross-over is not obvious in the observed q range for the cut in K-L plane, suggesting that, in the K-L plane, the HDS is much stronger. This anisotropy of the HDS along a^* and b^* already can be seen in Fig.(4.9) by comparing the diffuse scattering intensities in H-L and K-L planes and it is demonstrated more clearly in Fig.(4.11) where two dimensional diffuse scattering pattern in the H-K plane is presented. The lobes of the HDS, extending roughly along $[0\ 1\ 1]$ direction in K-L plane(Fig.(4.9)a) and $[1\ 0\ 1]$ direction in H-L plane(Fig.(4.9)b), manifest themselves as peak structures in H-K plane shown in Fig.(4.11). Apparently, the “peaks” along the b^* direction are much stronger than those along the a^* direction.

Obviously, this anisotropy of the HDS along a^* and b^* is related to the orthorhombic structure of our sample at low temperature. Indeed, our temperature dependent studies reveal the intimate relations between the anisotropy of the strain field associated with the Sr dopants and the orthorhombicity of the lattice. In Fig.(4.12), the line scans of $[0, K, 22.15]$ and $[H, 0, 22.15]$ are plotted as a function of temperature. At low temperatures, the intensities of the line scans in H-L plane are much lower than those in K-L plane, indicating strong anisotropy in the diffuse scattering intensities along $\mathbf{a}^*$ and $\mathbf{b}^*$ directions. As a function of increasing temperature, the anisotropy becomes smaller and almost invisible at $T = 250K$, which is close to the HTT-LTO transition temperature($\sim 280K$ [55]) for 8% doping. During the increasing of temperature from $7K$ to $250K$, the orthorhombicity of

the LSCO lattice, $\frac{b-a}{b+a}$, decreased from 0.0031 to 0.0003 by a factor of 10.

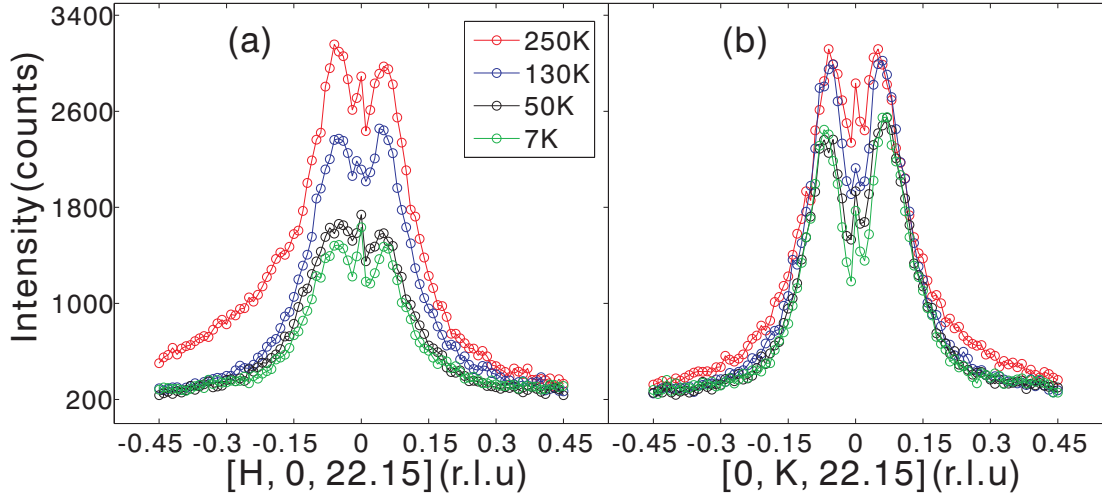


Figure 4.12 Temperature dependent H and K scans across $[0, 0, 22.15]$. (a) and (b) share the same color scheme. Low temperature data shows big intensity ratio between K and H cuts. The ratio decreases as temperature is increased and almost approaches 1 at $T=250K$.

As shown in Eqn.(3.25), the symmetry of the HDS is determined by both the elastic dynamic matrix and the dipole force tensor. At $\sim 7K$, the lattice constants a and b are determined to be $5.234\text{\AA}$ and $5.357\text{\AA}$ respectively from our experiments. Due to the slightly orthorhombic structure, the elastic dynamic matrix is anisotropic along the $\mathbf{a}$ and $\mathbf{b}$ directions. For example, the reported elastic constants[56] c_{11} and c_{22} are 1.722 and 1.716 in unit of $10^{12}dyn/cm^2$. Even though they are different, the difference is fairly small($\sim 0.35\%$). Later we will show that it is mainly the anisotropy of the dipole force tensor that causes the observed strong anisotropy of the HDS.

4.4 Data fitting and analysis

As the nature of the observed diffuse scattering is clarified in previous section, we fitted the total diffuse scattering around several Bragg peaks with HDS+TDS model. The

$1/q^2$ dependence of the HDS intensities demonstrated in previous section suggests that the formulation of the HDS for random dopant distribution in section **3.3.5** is applicable here.

From Eqn.(3.45) and Eqn.(2.20), the total diffuse scattering intensities can be written as,

$$I_{diff}(\vec{Q}) = \frac{N}{M} \left| \sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} \right|^2 \left(c(1-c) \left| \sum_{\alpha\beta} Q_\alpha \mathbb{D}_{\alpha\beta}^{-1} \sum_\gamma P_{\beta\gamma} q_\gamma \right|^2 + \frac{\hbar}{2} \sum_j \frac{[\vec{Q} \cdot \tilde{e}(\vec{q}j)]^2}{\omega(\vec{q}j)} \coth \frac{\hbar\omega(\vec{q}j)}{2KT} \right) \quad (4.2)$$

where the TDS is calculated based on continuum elastic theory. Since the data to be fitted was collected at $\sim 7K$ at which the populations of high energy phonon modes very small, we neglect the diffuse scattering contribution from optical-type lattice vibrations.

In most cases, the existence of TDS is unfavorable, as it “contaminates” the desired signals by reducing the signal to background ratio. But here, for the HDS analysis, the TDS is very important. It is always a big problem for X-ray scattering to normalize the measured intensity against the intensity of the incident beam because they are usually measured by detectors with different efficiency. This cannot be avoided since there is an order of magnitude difference in intensity between the two and there is no single detector to cover the large intensity range. Thus, one always needs a scaling factor when comparing the calculated intensity with that measured. Also, as shown in Eqn.(4.2), the HDS we study here is scaled by the total number of unit cells N , which is undetermined and usually merged into the overall scaling factor. If the measured intensities are pure HDS, the P matrix can not be determined on an absolute scale but with an unknown constant factor. The existence of TDS resolves this ambiguity. From Eqn.(4.2), we see that the TDS shares the same scaling factor with HDS. The second term in the bracket of Eqn.(4.2), which is

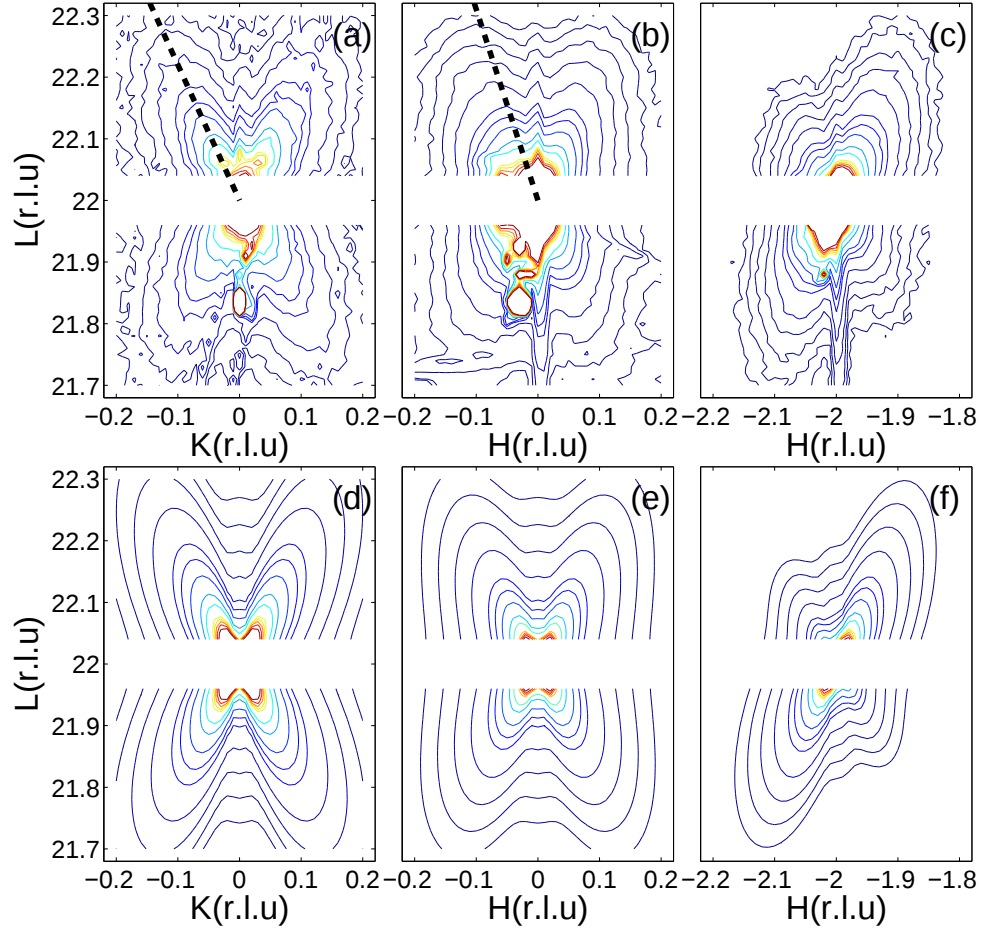


Figure 4.13 (a): 2-D mesh in the **K-L** plane around (0 0 22). (b): 2-D mesh in the **H-L** plane around (0 0 22). (c): 2-D mesh in the **H-L** plane around (-2 0 22). (d), (e) and (f) are the fitting results with HDS+TDS model accordingly.

from TDS, can be precisely calculated since the elastic constants needed to determine $\tilde{e}(\vec{q}j)$ and $\omega(\vec{q}j)$ have been well measured and documented. Thus, the TDS serves as a built-in reference to the HDS and the P matrix can be determined on an absolute scale.

In our fitting, we use the elastic constants measured by A.Migliori *et al.*[56]. The mass density of LSCO needed to determine the elastic dynamic matrix defined in Eqn.(3.9) is calculated to be $7.1g/cm^3$ with the tabulated atomic weights and the measured lattice

constants. The fitting was done around several Bragg peaks, namely $(0, 0, 22)$, $(-2, 0, 22)$ and $(0, 2, 22)$, simultaneously. The fitted total diffuse intensity, comparing with the measured diffuse pattern shown in Fig.(4.9), is shown in Fig.(4.13).

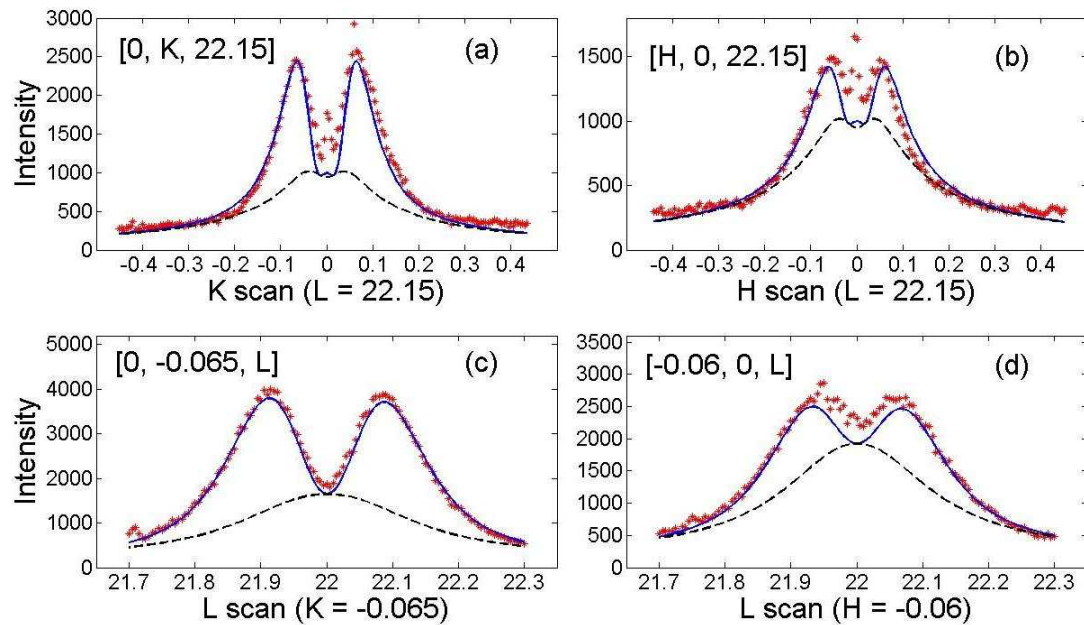


Figure 4.14 Asterisk lines are the measured diffuse scattering intensities along several lines in the reciprocal space. Solid lines are the calculated total diffuse intensities with fitted parameters. Dashed lines show the TDS contribution.

The measured intensities along several lines in the reciprocal space, together with the fitted curves, are shown in Fig.(4.14) to illustrate the quality of our fitting. The TDS is also shown in Fig.(4.14)(the dashed lines) to indicate the relative contributions from HDS and TDS to the total diffuse scattering.

As the result of our fitting, the P matrix is determined to be,

$$P = \text{sign} \begin{pmatrix} 6.93 & 0 & 0 \\ 0 & 10.54 & 0 \\ 0 & 0 & 1.06 \end{pmatrix} 10^{-19} N \cdot m$$

Even though the values of the P matrix elements can be determined on an absolute scale with the reference from TDS, there is still a overall sign of the P matrix which can not be determined because the HDS is proportional the the modulus square of the P matrix. This overall sign has it own importance because it tells whether the local lattice is compressively or expansively distorted, which will be further discussed later.

The determined P matrix shows some distinct characters. First, all the off-diagonal elements are zero from fitting. Second, the diagonal elements suggest that the strain fields are strongly anisotropic.

Before addressing these two issues in detail, we would like to clarify the origin of the observed HDS: is it due to the Sr dopant induced local lattice distortion or due to the proposed polarons as discussed in the introduction of this chapter? If the observed HDS is due to polarons, the strong anisotropy of the HDS along **a** and **b** directions suggests that the holes are dressed with phonons in an anisotropic way. It is hard to believe that, in a slightly orthorhombic lattice with the orthorhombicity to be only 0.0031 at $\sim 7K$, the holes are strongly anisotropically dressed. Also, this anisotropic dressing of the carriers will inevitably make the hoping of the carriers to be strongly anisotropic along **a** and **b** directions, which, to our knowledge, has never been reported in literature. Further, if the holes are ansitropically dressed with phonons due to unknown mechanism, it is difficult to

explain the disappearance of the **a-b** anisotropy of the HDS at the LTO-HTT structural phase transition temperature. Based on the above arguments, we believe the HDS observed in our experiments is due to the Sr dopant induced local lattice distortion.

The zero values of the off-diagonal elements of the P matrix reflects the symmetry of the defect centers. From Fig.(4.2), we can tell that the crystal structure has mirror symmetry about the **b-c** plane respect to the La sites, on which the Sr atoms will reside upon doping. Due to this mirror symmetry, every atom with coordinate (x,y,z) respect to the Sr site has its counter part at $(-x,y,z)$ unless $x=0$. Based on the same symmetry argument, the Kanzaki forces exerted on the pairs should be (F_1, F_2, F_3) and $(-F_1, F_2, F_3)$. The elements of the P matrix, as defined in Eqn.(3.37), are given by $\sum_{l'k'} F_{l'k'\beta} R_{l'k'\gamma}$. The force dipoles associated with the individual atoms of the pair cancel each other when $\beta = 1$ and $\gamma = 2$ or 3 . This is also true when $\gamma = 1$ and $\beta = 2$ or 3 . For those atoms with x coordinate to be zero, which have no paring atoms, the **a** direction components of the Kanzaki forces are also zero. They, again, have zero contributions to the off-diagonal elements $P_{1\gamma}$ and $P_{\beta 1}$. Thus, all the off-diagonal elements related to **a** direction are zero due to the mirror symmetry about the **b-c** plane with respect to the Sr dopants.

Interestingly, the above symmetry argument can not justify the zero values of P_{23} and P_{32} because the rotation of the CuO_6 octahedra about the **a** direction breaks the mirror symmetry about the **a-c** plane. The fact that P_{23} and P_{32} are zero given by our fitting might be explained by the following two possible reasons. The deviation from the mirror symmetry is actually not big since the rotation of the CuO_6 octahedra is ~ 3.5 degrees[2] at low temperature. Thus the resulted non-zero values of the off-diagonal elements might be too small to be resolvable in our X-ray diffuse scattering experiments. The other possibility

is that the rotation of the CuO_6 octahedra, which is established globally, might be locally suppressed near the Sr dopants. This explanation is more relevant to us because it is related to the role of the Sr dopants in the HTT to LTO structural transition and the strong **a-b** anisotropy of the strain fields we observed here.

At this point, it is important to clarify the relation between the dipole force tensor matrix P and the strain in the crystals to avoid any confusion. The experimentally observed quantity, the HDS, is expressed in term of the lattice distortion vector $\vec{u}_{lk}$ in Eqn.(3.20). In Eqn.(3.38), we show that the long range elastic lattice distortion can be presented in terms of the elastic dynamical matrix and the the dipole force tensor matrix. It is the dipole force tensor matrix **and** the elastic dynamic matrix together that determine the lattice distortion pattern. Thus, the lattice strain is related to but not determined by the dipole force tensor matrix P along. Only when the studied lattice is isotropic, does the P matrix directly determine the directional properties of the strain. For other cases, the detailed elastic properties of the lattice need to be considered.

The LSCO is of perovskite type with layered structure, as shown in Fig.(4.2). It is generally agreed that the inter-layer interaction is much weaker than intra-layer interaction for all cuprate families. Thus the effect of the Sr dopants on the local lattices is expected to be relatively weaker along **c** direction. This explains the smaller value of P_{33} , Comparing with P_{11} and P_{22} . While the big difference between P_{11} and P_{22} can not be explained following the same simple argument. For the sample we studied here, $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$, the crystal structure is tetragonal at room temperature and at $7K$ it is slightly orthorhombic($\frac{b-a}{b+a} \sim 0.0031$) due to the CuO_6 octahedra rotation. If we assume the local structural environment for the Sr dopants is the same as that of the La atoms in the

average lattice, this slight orthorhombicity seems not enough to be responsible for the big difference between P_{11} and P_{22} . Also, it can not give a direct explanation to why P_{22} is greater. In order to explain our fitting results, a microscopic consideration is needed.

The importance of the Sr dopants to the LSCO crystal structure has long been noticed. The structural phase diagram for LSCO from Keimer *et al.*[2] is shown in Fig.(4.1). The parent compound, La_2CuO_4 has a HTT to LTO structural phase transition at $\sim 530\text{K}$. This phase transition is due to the bond-length mismatch in different layers. J. B. Goodenough and A. Manthiram have used the Goldsmidt tolerance factor, $t = (La - O)/\sqrt{2}(Cu - O)$, to measure the bond-length matching[38]. At lower temperatures, $t < 1$ and the LaO layers are under tension and the CuO_2 sheets under compression. Nature adjusts to this mismatch by a cooperative tilting of the CuO_6 octahedra below transition temperature. As a result, the CuO_2 sheets are buckled and the bending of Cu-O-Cu bond from 180 degrees relieves the compressive stress on the CuO_2 sheets. Since the ionic radius of Sr^{2+} is larger than that of La^{3+} , the introduction of Sr dopants increases the average t value and helps to release the tension. Thus the structural phase transition temperature rapidly decreases as a function of increasing Sr concentration. This dopant effect on the structural transition is more evidenced by comparing LSCO with the other closely related compound $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. In $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, the ionic radius of Ba^{2+} is even larger. J. D. Axe *et al.*[57] showed that the structural transition temperature is further suppressed, considering the same dopant concentration.

The above macroscopic experiment results clearly show that the local lattice distortion induced by the Sr dopants has the tendency to oppose the structural phase transition. In the regime where the macroscopic LTO phase is established, it is conceivable that locally

the cooperative CuO_6 octahedra rotation is suppressed or destroyed near the Sr dopants. Indeed, local structural deviation from average crystal structure in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ has been observed by many other experiments[58, 59, 60, 61]. For example, from their extended X-ray absorption fine structure(EXAFS) data measured on the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ sample, A. Bianconi *et al.*[58] concluded that there were two different Cu-O planar bond lengths and the probability of the longer bond length is about 16% at low temperature.

From our point of view, in the LTO phase where the **a** axis CuO_6 octahedra rotation with atomic displacements mainly along the **b** direction is globally established, locally the Kanzaki forces from the Sr dopants are against the HTT to LTO transition. Since the atomic displacements due to CuO_6 octahedra rotation are along the **b** direction, the counter forces from the Sr dopants are expected to be stronger along this direction. This scenario agrees with the experimentally observed strong anisotropy of the diffuse scattering and our fitting results which give a much greater P_{22} than P_{11} .

Since the observed HDS is due to long range lattice strain, our X-ray diffuse scattering experiments can not provide detailed information about how exactly the unit cells containing the Sr dopants are distorted. Since the elements of the P matrix are the summations of the dipole force tensors over all the surrounding atoms, they are averaged quantities. On the other hand, we are able to reconstruct the strain fields associated with the Sr dopants based on the observed HDS and the fitted P matrix. This will give us information about the elastic lattice distortion in nano-scale, which might be more relevant to the high temperature superconductivity since the superconducting coherent length is of this scale. Furthermore, the STM observed electronic inhomogeneity mentioned at the beginning of this chapter is also of nano-scale. In the next section, a detailed calculation

of the elastic lattice distortion in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ will be performed. We will discuss our results in connection with the STM observations to try to understand the origins of the electronic inhomogeneity in the CuO_2 plane.

4.5 The elastic lattice distortion pattern

The single defect induced lattice distortion has been expressed in Eqn.(3.19) in terms of Kanzaki forces. Following that, we neglected the optical-type components of the lattice distortion, which is much smaller than the acoustic-type components, and translated the lattice distortion calculation into the elastic continuum theory language. Then we showed that the X-ray diffuse scattering from the long range strain fields, the HDS, can be expressed in terms of elastic dynamic matrix and the force dipole matrix in Eqn.(3.39). In this section, we will still keep the acoustic approximation and calculate the elastic lattice distortion pattern based on the Kanzaki force dipole matrix P fitted in the previous section.

From Eqn.(3.19) and Eqn.(3.28), the acoustic component of lattice distortion vector $u_{lk\alpha}$ can be written as,

$$u_{lk\alpha} = \frac{1}{N} \sum_{\vec{q}, \beta} \left(\sum_j \frac{v_\alpha(\vec{q}j) v_\beta^*(\vec{q}j)}{\omega_{\vec{q}j}^2} \sum_{l'k'} F_{l'k'\beta} e^{-i\vec{q} \cdot \vec{R}_{l'k'}} e^{i\vec{q} \cdot \vec{R}_{lk}} \right) \quad (4.3)$$

where $\vec{v}(\vec{q}j)$ are the eigenvectors of the elastic dynamic matrix as defined in Eqn.(3.25). Detailed definitions of each term and their indexes can be found in section **3.3.4**. The summation over the acoustic phonon branch index j is given in Eqn.(3.34). As a result, the

above equation becomes,

$$u_{lk\alpha} = \frac{1}{N} \sum_{\vec{q}, \beta} \left(\frac{1}{M} \mathbb{D}_{\alpha\beta}^{-1} \sum_{l'k'} F_{l'k'\beta} e^{-i\vec{q} \cdot \vec{R}_{l'k'}} e^{i\vec{q} \cdot \vec{R}_{lk}} \right) \quad (4.4)$$

Following Eqn.(3.37) and Eqn.(3.38), we again generalize the summation of the Kanzaki forces to be the dipole force tensor.

$$u_{lk\alpha} = \frac{1}{N} \sum_{\vec{q}} \left(\sum_{\beta\gamma} \frac{-i}{M} \mathbb{D}_{\alpha\beta}^{-1} P_{\beta\gamma} q_{\gamma} e^{i\vec{q} \cdot \vec{R}_{lk}} \right) \quad (4.5)$$

Since the single domain grain illuminated by our X-ray beam is about tens of micron in size, the phonon wavevector $\vec{q}$ can be regarded as a continuous quantity. Thus, we can write the summation on $\vec{q}$ as a three dimensional integration over $\vec{q}$.

$$u_{lk\alpha} = \frac{V}{(2\pi)^3 N} \int_q \sum_{\beta\gamma} \frac{-i}{M} \mathbb{D}_{\alpha\beta}^{-1} P_{\beta\gamma} q_{\gamma} e^{i\vec{q} \cdot \vec{R}_{lk}} d\vec{q}^3 \quad (4.6)$$

where V is the total volume illuminated by the X-ray beam. N has been defined as the total number of the unit cells. Thus we have $\frac{V}{N}$ to be the volume of a single unit cell. With M to be the total mass of a unit cell, $\frac{V}{NM}$ ends up to be the inverse of the sample mass density ρ . For the elastic lattice distortion, individual atoms within a unit cell will not be distinguished. Thus we neglect the atom index k .

$$u_{l\alpha} = \frac{-i}{(2\pi)^3 \rho} \int_q \sum_{\beta\gamma} \mathbb{D}_{\alpha\beta}^{-1} P_{\beta\gamma} q_{\gamma} e^{i\vec{q} \cdot \vec{R}_l} d\vec{q}^3 \quad (4.7)$$

The integration is over the Brillouin Zone in the reciprocal space. Since $\mathbb{D}$ contains only quadratic terms of q (Eqn.(3.25)) and P matrix is unrelated to q , the above integration will

give real results, which agrees with the fact that the lattice distortion should be real.

Once the dipole force tensor matrix P is known, the elastic lattice distortion induced by single defect can be calculated by Eqn.(4.7). Unfortunately, we still have the sign problem for the P matrix fitted in previous section. In previous section, we have discussed the general role of the Sr dopants in the HTT to LTO structural phase transition for LSCO. Since the ionic radius of Sr^{2+} is larger than that of La^{3+} and it is less positively charged, the Sr atoms are believed to locally expand the LaO layers to relieve the inter-layer stress. Thus it is conceivable that the local distortion induced by Sr dopants are of expansive character with the Kanzaki forces exerted on the nearby atoms to be along the atom displacement direction. This scenario will give a positive sign to the fitted P matrix. We will take this to be true in the following discussion.

Based on Eqn.(4.7) and the P matrix determined from previous section, we calculated the elastic distortion near the Sr dopants. In Fig.(4.15), we show the distortion pattern in the **a-b** plane. The red dots indicate the mass center of the individual unit cells. In order to make the distortion pattern visible in the plot, the distortion vectors $\vec{u}_i$ are magnified by a factor of 100. The distortions near the Sr dopants are of the order of picometres(see discussion below) and decrease down quickly in a $\frac{1}{R^2}$ manner away from the Sr centers. Five picometres is about 1% of the unit cell lengths along **a** and **b** directions. Thus, even though the the distortion vectors $\vec{u}_i$ are scaled up by a factor of 100, only the distortions of the lattice very near to the Sr dopants can be clearly seen in the plot.

The elastic lattice distortion pattern in the **a-b** plane presented in Fig.(4.15) clearly shows the anisotropic nature of the strain fields. The distortion along **b** direction is much stronger than that along **a** direction, which has been expected from the the experimen-

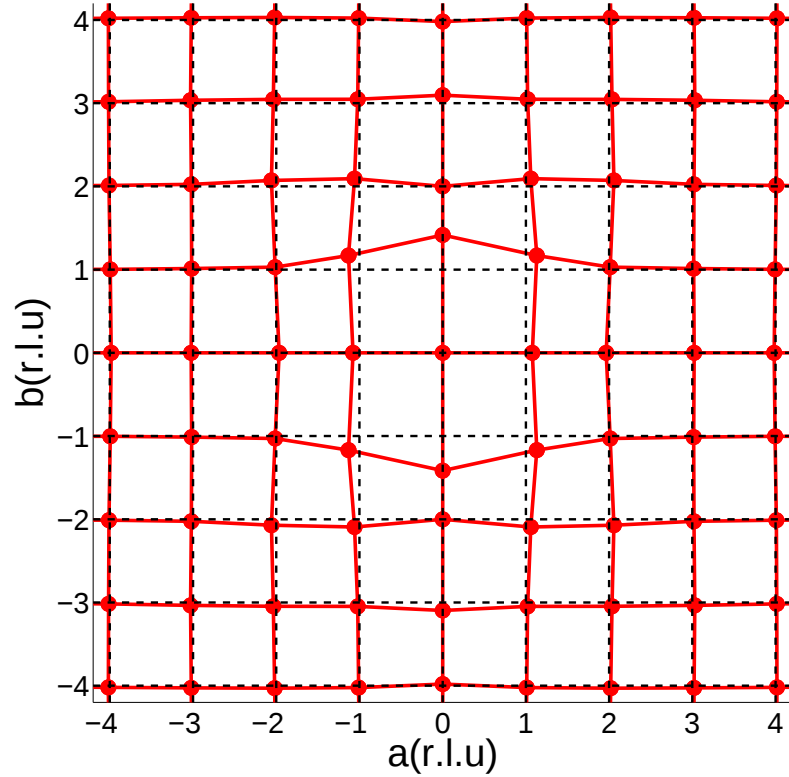


Figure 4.15 Red dots: the mass centers of the individual unit cells. Black dashed lines: the original lattice grid without distortion.

tally observed anisotropy of the X-ray diffuse scattering pattern(Fig.(4.9), Fig.(4.10) and Fig.(4.11)). In the following, we will quantitatively discuss the details of the calculated elastic lattice distortion.

For the convenience of the discussion, we write the unit cell index l explicitly as (l_a, l_b, l_c) with the three indexes to be along **a** , **b** and **c** directions. From the relative displacements of the adjacent unit cells, we can estimate the compression or expansion of individual unit cells. For example, $u_{(l_a+1, l_b, l_c), a} - u_{(l_a-1, l_b, l_c), a}$ gives the compression or expansion of the (l_a, l_b, l_c) -th unit cell along **a** direction. Based on our calculation, the center unit cell containing the Sr dopant expands along **a** direction by $0.008\text{\AA}$ and **b** direction by

0.045Å. Along **c** direction, it is contracted by 0.016Å. Due to the three dimensional elastic coupling, the lattice distortion is not monotonic along fixed direction and it oscillates near the Sr dopants. Thus, along fixed direction, some unit cells are expanded and some are compressed. For example, from Fig.(4.15), we can tell that along **b** direction the (0, 0, 0)-th unit cell is expanded, the (0, 1, 0)-th unit cell is compressed and the (0, 2, 0)-th unit cell is again expanded. Nevertheless, the amplitude of the compression or expansion of the nearest neighbors to the center unit cell are of the same order as that of the unit cell containing the Sr dopant and again, it decreasing down a $\frac{1}{R^2}$ manner away from the Sr center.

Based on the linear compressibility coefficients for LSCO measured by G. Oomi *et al.*[62], 0.01Å change in the unit cell size is equivalent to a local pressure of about 1 GPa. In the introduction to this chapter, we have referred to many experimental observations[40, 41, 42, 43] which have shown that the pressure on bulk cuprate crystals has strong effect on the high temperature superconductivity. In the hydrostatic pressure experiments[40, 41], T_c can be tuned by pressure of the order of 0.1K/GPa. The uniaxial pressure experiments[42, 40, 43] show that the effect of pressure on T_c can be an order higher and shows strong anisotropic behavior. Thus, the local pressure of the order of 1GPa deduced from our X-ray diffuse scattering data should have drastic effect on the superconductivity locally. More direct link between the elastic distortion we observed and effect on the local superconducting properties in LSCO can be established by examine the epitaxial strain experiments on LSCO thin films[63]. J.-P.Locquet *et al.* demonstrated that the T_c was doubled for epitaxial grown $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ on SrLaAlO_4 substrate with an in-plane compressive strain to be 0.63%. For thin films gown on SrTiO_3 with an in-plane expansive strain to be 0.54%, T_c was decreased

by half. For these two cases, the unit cell lengths along **a** and **b** directions are decreased or increased by 0.033 or 0.028 Å respectively. The lattice expansion or compression near the Sr dopants we calculated is comparable with these values.

The above discussion suggests that the Sr dopants induced local elastic lattice distortion may play the leading role in the nano-scale electronic inhomogeneity observed on LSCO by T.Kato *et al.*[39]. Similarly, the dopant induced local structural distortions might also be the sources of the electronic inhomogeneity observed in other cuprate families, such as the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ compound[15]. The strong in-plane anisotropy of the strain due to Sr dopants we observed here suggests the superconducting gap width distribution will be also spatially anisotropic if the lattice distortion plays the major role for the electronic inhomogeneity. To observe this anisotropy, very high resolution STM experiments are required because the resulting anisotropy in the spatial gap width distribution might be smeared out if the STM tips average the signal from several adjacent unit cells.

4.6 Summary

In this chapter, the results of our X-ray diffuse scattering experiments on underdoped $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ high temperature superconductor were discussed. On top of the thermal diffuse scattering, diffuse scattering with strong anisotropy from a different origin was observed at low temperature. We showed that this anisotropic diffuse scattering can be well described by the HDS due to uncorrelated single defects. We believe it is the scattering from the long range strain-type lattice distortion induced by the Sr dopants.

Temperature dependent studies show that the in-plane anisotropy of the observed HDS is closely related to the HTT to LTO structural phase transition of $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$

at $\sim 280K$ [2]. The anisotropy decreases with increasing temperature and becomes almost invisible at $T = 250K$. We related the observed anisotropy to the role of the Sr dopants in the HTT to LTO structural phase transition. Generally, the introduction of Sr dopants suppresses the structural phase transition[2, 38]. At low temperature when the macroscopic LTO phase is established, the Sr dopants might locally destroy the cooperative CuO_6 octahedral rotation by exerting strong Kanzaki forces to the surrounding atoms along $\mathbf{b}$ direction since the cooperative CuO_6 octahedra rotation tends to displace the atoms along this direction.

With the parameters obtained by fitting to the overall diffuse scattering data with the HDS+TDS model, we reconstructed the elastic lattice distortion pattern. Our calculated results show that the Sr dopant induced lattice distortion is fairly strong. The unit cells very close to the Sr dopant centers are expanded or compressed in the order of $0.01\text{\AA}$, which is equivalent to a local pressure variation in the order of 1GPa calculated with the measured compressibility coefficients for LSCO[62]. The pressure experiments[40, 41, 42, 43] on bulk cuprate crystals and the epitaxial strain experiments[63] on cuprate thin films have shown significant effect of the pressure and strain on the superconducting transition temperature T_c . By comparing our results with the conclusions from these experiments, we suggest that the Sr dopant induced local lattice distortions play the leading role in the electronic inhomogeneity observed in the STM experiments[39].

This chapter contains materials in

- X. Liu, E. Blackburn, Z. Islam, S. K. Sinha, R. J. McQueeney and S. Wakimoto, “Local lattice distortion in underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor”, in preparation(2009)

5

X-ray Diffuse Scattering from optimally doped $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$

High temperature superconductivity in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ is realized by doping the parent Mott insulator $\text{YBa}_2\text{Cu}_3\text{CuO}_6$ with extra oxygen. The oxygen dopants go to the Cu-O chains in the so-called chain planes(labeled as O(1) in Fig.(5.1)). At high temperatures(way above room temperature), $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ has a tetragonal structure and there are two equivalent O(1) sites. Thus, the whole CuO plane can be viewed as composed of three interpenetrating square lattices, one occupied by Cu ions(Cu(1)) and the other two by oxygen ions(Fig.(5.1b)). At high temperature, both the two oxygen square lattices are randomly occupied, which gives rise to an average tetragonal structure. As the temperature is lowered, the oxygen ions tend to populate preferentially one of the two sublattices, thus forming -Cu-O-Cu- chains. The formation of the CuO chains breaks the tetragonal symmetry and drives the crystal structure to be orthorhombic(Fig.(5.1a)).

The ordering of oxygen dopants in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ to form CuO chains has

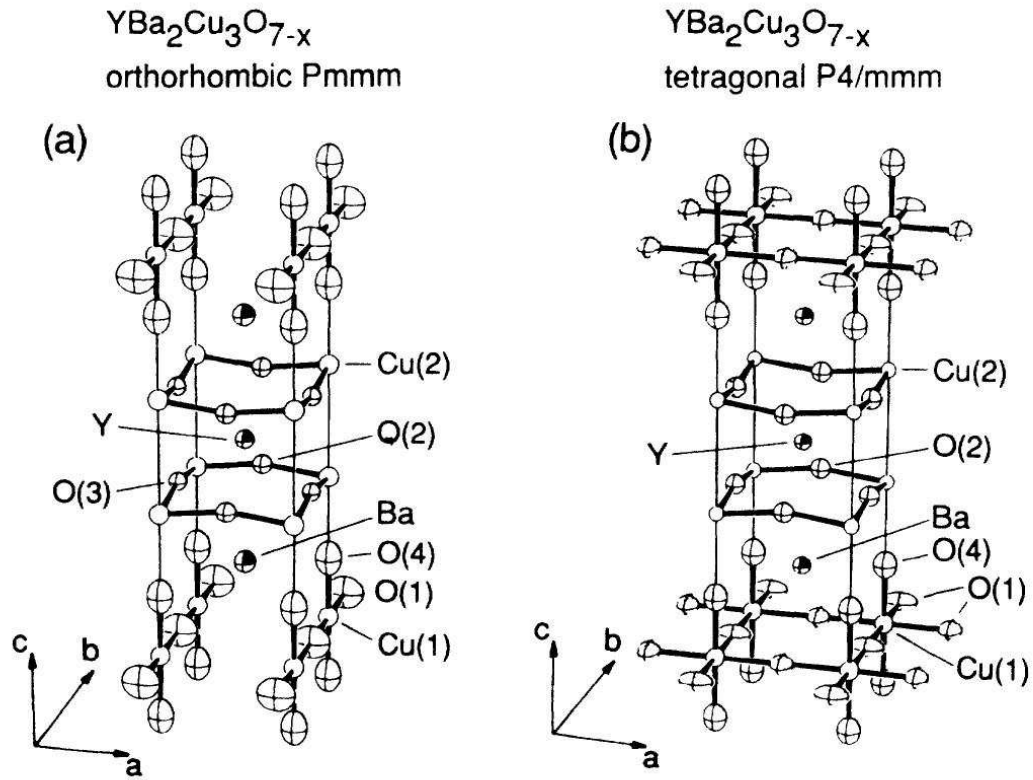


Figure 5.1 (a) Orthorhombic and (b) tetragonal structures of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. From J.D.Jorgensen *et al.*[4]

been experimentally observed by many different groups on samples with different oxygen contents[4, 64, 65, 66, 5]. The diffraction experiments show that, with different oxygen stoichiometry, the ordered CuO chains form different phases. The formation of superstructure phases has been further theoretically studied by D.de Fontaine *et al.*[30] and N.H.Andersen *et al.*[5]. The idealized structural phases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ for “good” stoichiometries are shown in Fig.(4.2)(From N.H.Andersen *et al.*[5]). When $x=0$, one of the oxygen sublattices is fully occupied by oxygen ions and the other sublattice is empty. Thus, fully occupied Cu-O chains, running along b directions, form throughout the crystal. This is denoted as “ORTHO-I” phase. The well known “ORTHO-II” phase is established around the center

composition $x=0.5$ with a cell-doubling structure, an alternate stacking of filled and empty chains. Other long range superstructure phases can form at “good” stoichiometries with $x \sim \frac{n}{m}$ (n and m are integers), as shown in Fig.(5.2). A more detailed and complicated structure phase diagram for $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ is given by D.de Fontaine *et al.*[67] based partly on calculations and partly on conjecture.

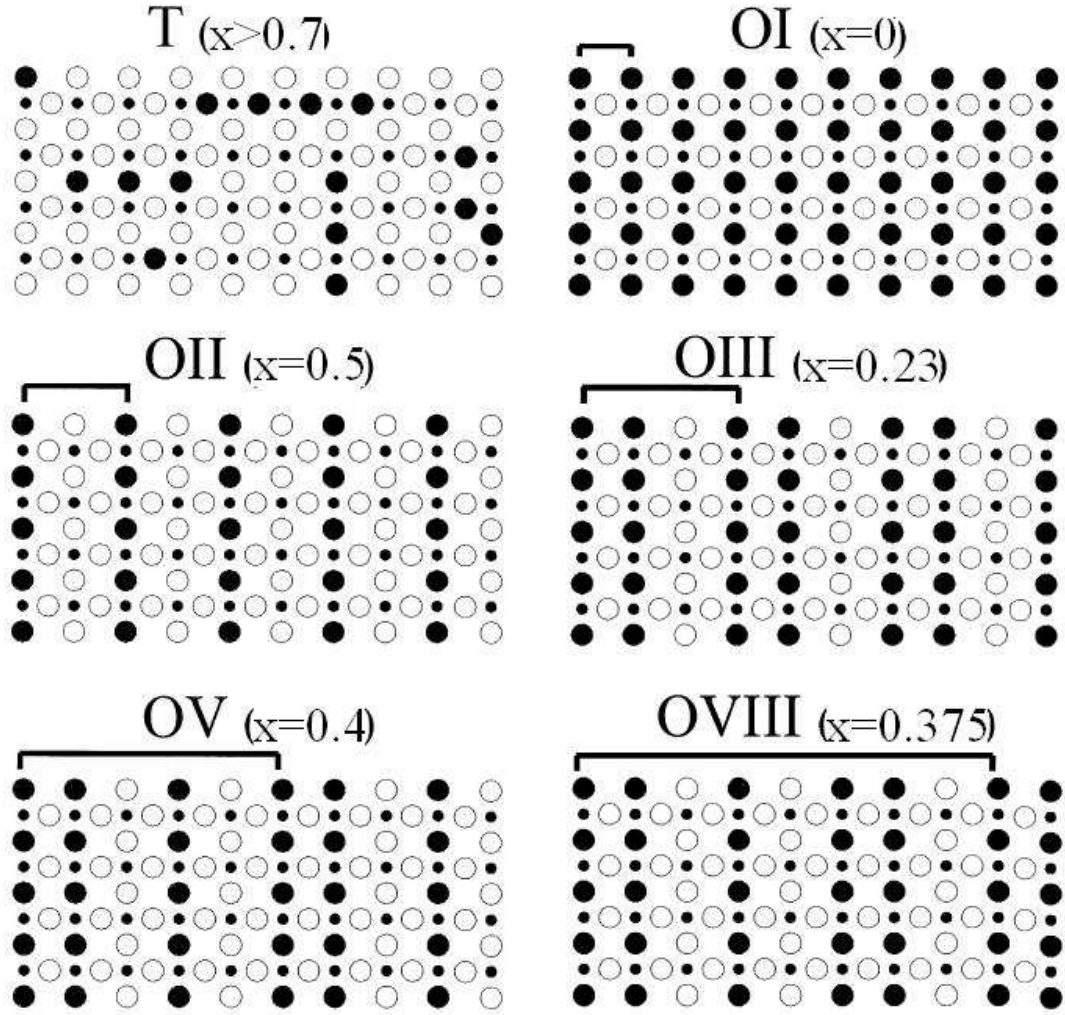


Figure 5.2 Idealized structural phases in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ from Monte Carlo simulations. Small dots: Cu; Big dots: O; Circles: empty oxygen sites. T is the tetragonal disordered phase. OI-OVIII stand for ORTHO-I to ortho-VIII orthorhombic phases. From N.H.Andersen *et al.*[5]

The oxygen ordering in the CuO chain planes has long been noticed to significantly affect the superconductivity properties in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$. It is found that the superconducting transition temperature T_c of YBCO samples quenched at high temperatures is reduced compared to the equilibrium value and increases with time when the sample is annealed at room temperature[68, 69, 70]. Equally, it has been observed that the oxygen ordering of quenched YBCO crystals increase with time[71, 72]. More interestingly, two plateau regions in the superconducting phase diagram of YBCO(Fig.(4.3)) were observed at the compositions where three dimensionally long-range-ordered ORTHO-I($x \sim 0$) and ORTHO-II($x \sim 0.5$) phases dominate. For YBCO samples with other compositions, the oxygen ordering and the formation of superstructure phases can be very complicated. When the composition deviates from “good” stoichiometries, the crystal inevitably develops multiple phases of short range order. This has been referred to by R.J.Cava *et al.*[6] to explain the observed broadening of the superconducting transition for $0.2 < x < 0.4$ (Fig.(4.3)).

Thus, the oxygen ordering in the CuO chain planes in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ provides the unique opportunity for the CuO_2 planes to interact with the charge reservoir layers with varying degrees of disorder and inhomogeneity. Unlike the inhomogeneity introduced by point-like defects in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the dopant-introduced inhomogeneity in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ is in the form of clusters of different phases with much larger sizes(larger than the superconducting coherent length in most cases). More drastic effects of the disorder in the charge reservoir layers to the superconductivity are expected.

From the X-ray scattering point of view, it is interesting to know how the lattice is affected when different superstructure phases are formed and to what extent the CuO_2 planes are structurally distorted. To address these issues, we carried out X-ray diffuse

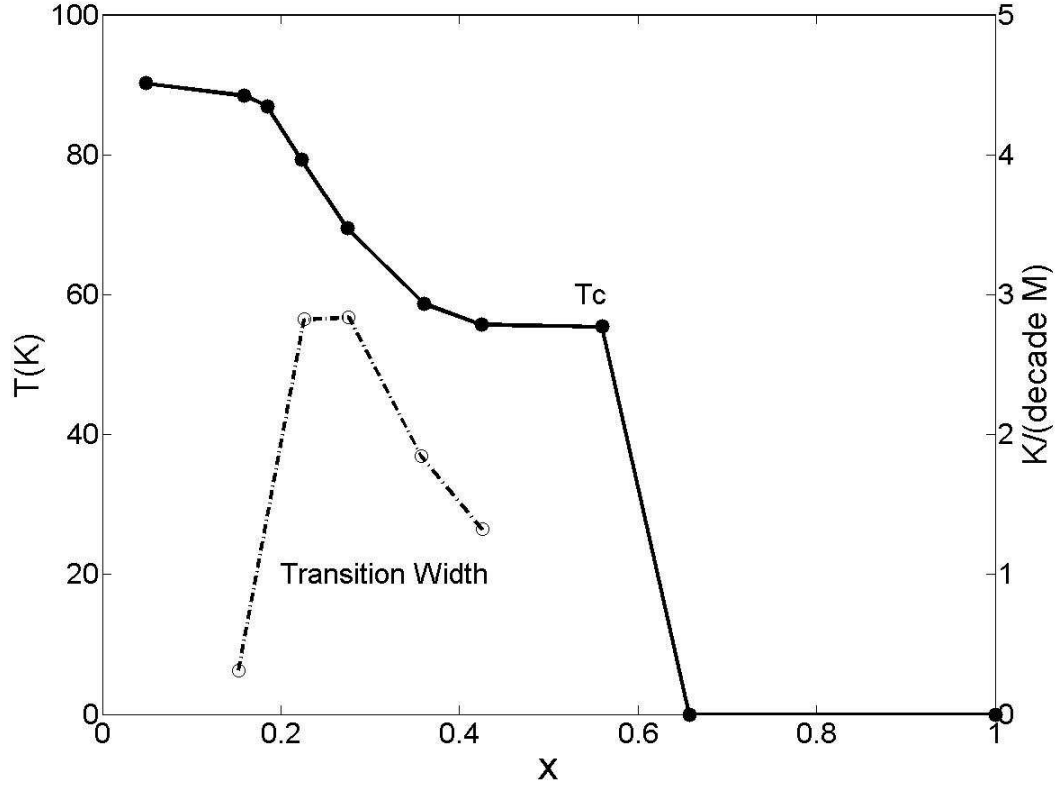


Figure 5.3 Solid line: superconducting transition temperature(T_c) v.s. doping for $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$. Dashed line: the transition widths for different oxygen compositions. The transition width is in Kelvins per decade of magnetization. The data is reprinted from R.J.Cava *et al.*[6]

scattering experiments on optimally doped $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$ with $x = 0.08$ [7]. A naive consideration based on the stoichiometry seems to suggest a superstructure of ORTHO-X phase with one out of ten CuO chains to be empty. The big distance between empty chains(10a) and the weak interaction between them[5] make this scenario unlikely. Indeed, our experiment results show that the empty chains cluster more closely to each other to form an “ORTH-IV” phase with a periodicity to be 4a along **a** direction.

In this chapter, we show our experimental observations of the formation of the “ORTH-IV” minority phase embedded in “ORTH-I” main phase in $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$.

A model is constructed to extract information about the local lattice distortion pattern in the “ORTHO-IV” minority phase and the associated long range lattice strain by fitting to the measured diffuse scattering data. The details of the model is given in Appendix A. Our quantitative analysis further revealed a $\mathbf{b}$ direction lattice modulation on top of the ORTHO-IV superstructure, confined within the ORTHO-IV minority phase region. The $\mathbf{b}^*$ direction wavevector of this new modulation matches the nesting vector of the Fermi surfaces of the one dimensional CuO chains, suggesting the $\mathbf{b}$ direction modulation is a Fermi surface induced effect.

5.1 Sample preparation and experiment setup

To study the structural inhomogeneity and multiple superstructure phase formation in $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$, a high-quality *detwinned* crystal in the optimally doped region with $x=0.08$ was chosen. The crystal was prepared by U. Welp at Argonne National Laboratory using a “self-flux” procedure similar to those described in Ref.[73] and Ref.[74]. The crystal is of a slab shape with dimension to be $\sim 1\text{mm} \times \sim 1\text{mm} \times \sim 130\mu\text{m}$. The largest crystal facet is perpendicular to crystal $\mathbf{c}$ axis. The crystal was annealed at 420°C in flowing pure O_2 for about a week and then was stress detwinned in flowing O_2 at the same temperature. Polarization-sensitive optical microscopy showed the sample is of a single twin domain. Magnetic susceptibility measurement showed the superconducting transition temperature to be 91.5K and the transition width to be $\sim 1\text{K}$.

The X-ray diffuse scattering experiments on this sample were performed on the X-Ray Operations and Research 4-ID-D beam line at the Advanced Photon Source(APS) at the Argonne National Laboratory. The experimental setup is the same as sketched in

Fig.(4.5). A high energy(36keV) X-ray beam was chosen for the experiments to ensure deep penetration into the bulk. At this energy, the X-ray attenuation length for $\text{YBa}_2\text{Cu}_3\text{O}_7$ is $\sim 230\mu\text{m}$ according to the *X-ray attenuation length table* provided by Center of X-ray optics at Lawrence Berkeley National Laboratory(http://henke.lbl.gov/optical_constants/atten2.html).

Our X-ray data confirmed that the crystal is of orthorhombic structure. At $\sim 7K$, the lattice constants, a , b and c , are determined to be $3.811\text{\AA}$, $3.911\text{\AA}$ and $11.68\text{\AA}$, respectively. Angular scans through the crystal Bragg peaks indicate the crystal mosaic spread is less than 0.03° , showing the good quality of our sample.

5.2 Diffuse scattering

The most prominent feature we observed in our X-ray diffuse scattering data is the series of broad satellite peaks at $\vec{G} \pm \vec{q}_0$ with $\vec{q}_0$ to be $(\frac{1}{4}, 0, 0)$, where $\vec{G}$ are the Bragg peaks as defined before. Figures 5.4(a)-5.4(d) show several $\mathbf{H}$ -scans along the $\mathbf{a}^*$ -direction for different integer values of $\mathbf{K}$ with $\mathbf{L}$ fixed to be 0. Most of the data shown in this chapter was taken at $\sim 7K$, unless specified otherwise. The observed series of $\vec{G} \pm \vec{q}_0$ satellite peaks indicate the existence of a superstructure modulation with $4a$ periodicity along the $\mathbf{a}$ -direction, which suggests the formation of the “ORTHO-IV” phase(*i.e.*, one out of every four CuO chains has no oxygen ions denoted by $\langle 1101 \rangle$) as predicted by theoretical calculations[30].

Comparing with the intensities of the Bragg peaks, the intensities of the $\vec{q}_0$ satellite peaks are some $\sim 10^6$ orders of magnitude weaker. Due to the weak intensities, those satellite peaks close to strong Bragg peaks are actually invisible in the $\mathbf{H}$ -scans. For example, on

both sides of the $(4, 0, 0)$, $(5, -1, 0)$ and $(6, -2, 0)$ Bragg peaks, we only see strong diffuse scattering tails extending from the Bragg peak centers. Due to the crystal symmetry of $\text{YBa}_2\text{Cu}_3\text{CuO}_{7-x}$, the intensities are expected to be strong for those Bragg peaks $(h, k, 0)$ whose $h + k$ values are even. As discussed in Chapter 2, the Bragg peak intensity is proportional to the modulus square of the unit cell structure factor. We have also shown that both the TDS and HDS have this proportional relation too (see details in Chapter 2).

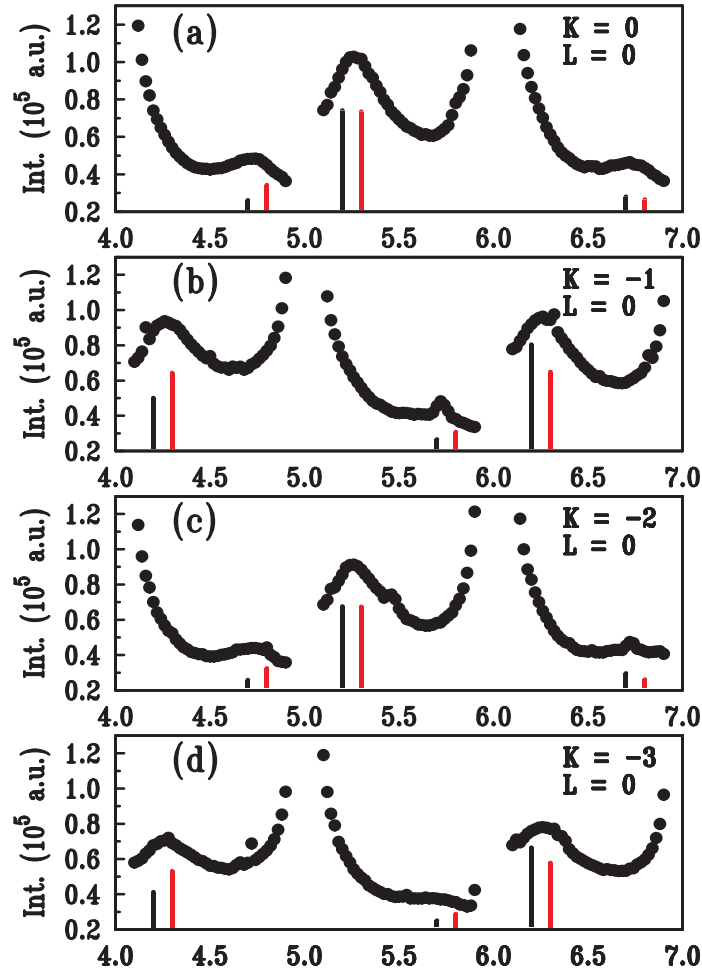


Figure 5.4 (a)-(d): **H**-scans for several integer values of **K** and **L**=0[7]. Satellite peaks are at $\vec{G} \pm \vec{q}_0$ with $\vec{q}_0 = (\frac{1}{4}, 0, 0)$. Vertical lines (displaced along **H** for clarity) compare the observed (black) and calculated (red) intensities corrected for geometric factors.

Thus, the TDS and HDS are also expected to be strong around those Bragg peaks and leave

the weak $\vec{q}_0$ satellite peaks to be unresolvable in the **H**-scans. Fortunately, the intensities of the satellite peaks have quite different $\vec{q}$ dependence comparing with that of TDS and HDS. We are able to resolve those satellite peaks in the **K**-scans across $\vec{G} \pm \vec{q}_0$. The **K**-scan across (4.25 0 0) satellite peak is shown in Fig.(5.5) as an example.

The intensities of the satellite peaks on both sides of a certain Bragg peak are highly asymmetric. For example, the (5,0 0)+(0.25, 0, 0) satellite peak is fairly strong but the (5,0 0)-(0.25, 0, 0) satellite peak is about 8 times weaker. In Chapter 3 we have discussed the general properties of X-ray diffuse scattering due to superstructure modulations. From Eqn.(3.4), we have,

$$I \propto \left| \sum_{nk} \tilde{f}_k e^{i\vec{Q} \cdot \vec{R}_{nk}} e^{i\vec{Q} \cdot \vec{u}_{nk}} \right|^2 \quad (5.1)$$

where n is the index of unit cells within a supercell and k is the index of atoms within a unit cell. If the amplitude of the superstructure modulation is small, $\vec{Q} \cdot \vec{u}_{nk}$ would be a small quantity. We expand $e^{i\vec{Q} \cdot \vec{u}_{nk}}$ to its first order,

$$I \propto \left| \sum_{nk} \tilde{f}_k e^{i\vec{Q} \cdot \vec{R}_{nk}} + \sum_{nk} i\vec{Q} \cdot \vec{u}_{nk} \tilde{f}_k e^{i\vec{Q} \cdot \vec{R}_{nk}} \right|^2 \quad (5.2)$$

The first summation vanishes at $\vec{G} \pm \vec{q}_0$. As a result, the intensities of the satellite peaks are scaling with $|\vec{Q}|^2$ with small modulation assumption. $|\frac{5.25}{4.75}|^2$ is about 1.22, which is much smaller than the observed ratio of the intensities of the two satellite peaks. Thus, the experimentally observed strong asymmetry of the satellite peak intensities indicates that small modulation assumption is not valid and the lattice is strongly distorted with the superstructure formation. This will be shown more clearly in our fitted superstructure distortion pattern(Fig.(5.10)).

The diffuse scattering intensity patterns are similar for **H** scans with the **K** values of the same parity. The **H** scans with the **K** values of different parity also seem to repeat if one of them is displaced along $\mathbf{a}^*$ direction by 1 r.l.u. To understand this parity relation, we examine again the proportional relation(5.1) but from another view. Substituting $\vec{Q}$ with $\vec{G} + \vec{q}_0$ and using the condition $e^{i\vec{G} \cdot \vec{R}_n} = 1$, we get,

$$I \propto \left| \sum_{nk} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} e^{i\vec{G} \cdot \vec{u}_{nk}} e^{i\vec{q}_0 \cdot (\vec{R}_{nk} + \vec{u}_{nk})} \right|^2 \quad (5.3)$$

Since the lattice modulation $\vec{u}_{nk}$ are small compared to the unit cell dimensions, we need only consider the leading effect on the satellite intensity caused by $e^{i\vec{G} \cdot \vec{R}_k}$ when the center Bragg peak changes from $\vec{G}$ to $\vec{G} + (0, 1, 0)$ or $\vec{G} + (0, 2, 0)$. Regarding the **K** value change, the ions within an unit cell can be classified into two groups whose positions along the **b** direction are displaced by $\frac{1}{2}b$ relative to each other (such as the relative positions of Cu and Ba, for example). By changing $\vec{G}$ to $\vec{G} + (0, 2, 0)$, $e^{i\vec{G} \cdot \vec{R}_k}$ are the same for both groups. Thus, the diffuse scattering patterns are similar as demonstrated in Fig.(5.4). If $\vec{G}$ changes to $\vec{G} + (0, 1, 0)$, $e^{i\vec{G} \cdot \vec{R}_k}$ is the same for one group but gives negative sign for the other group. Thus, the scattering from two groups becomes destructive if it is originally constructive around $\vec{G}$, or vice versa. The negative sign seems to be compensated by moving $\vec{G}$ with another step along $\mathbf{a}^*$ direction to $\vec{G} + (0, 1, 0) + (1, 0, 0)$, which indicates that the main contributors to the satellite intensities are also relatively displaced from each other along **a**-direction by $\frac{1}{2}a$. The parity relation of the diffuse satellite peak intensities discussed above impose strong constraints on our fitting, which will be discussed later.

In Fig.(5.5), scans along **K** and **L** directions across the satellite peaks are shown. In the **K**-scans, those satellite peaks near strong Bragg peaks, which are unclear in the

H-scans in Fig.(5.4) now can be clearly seen.

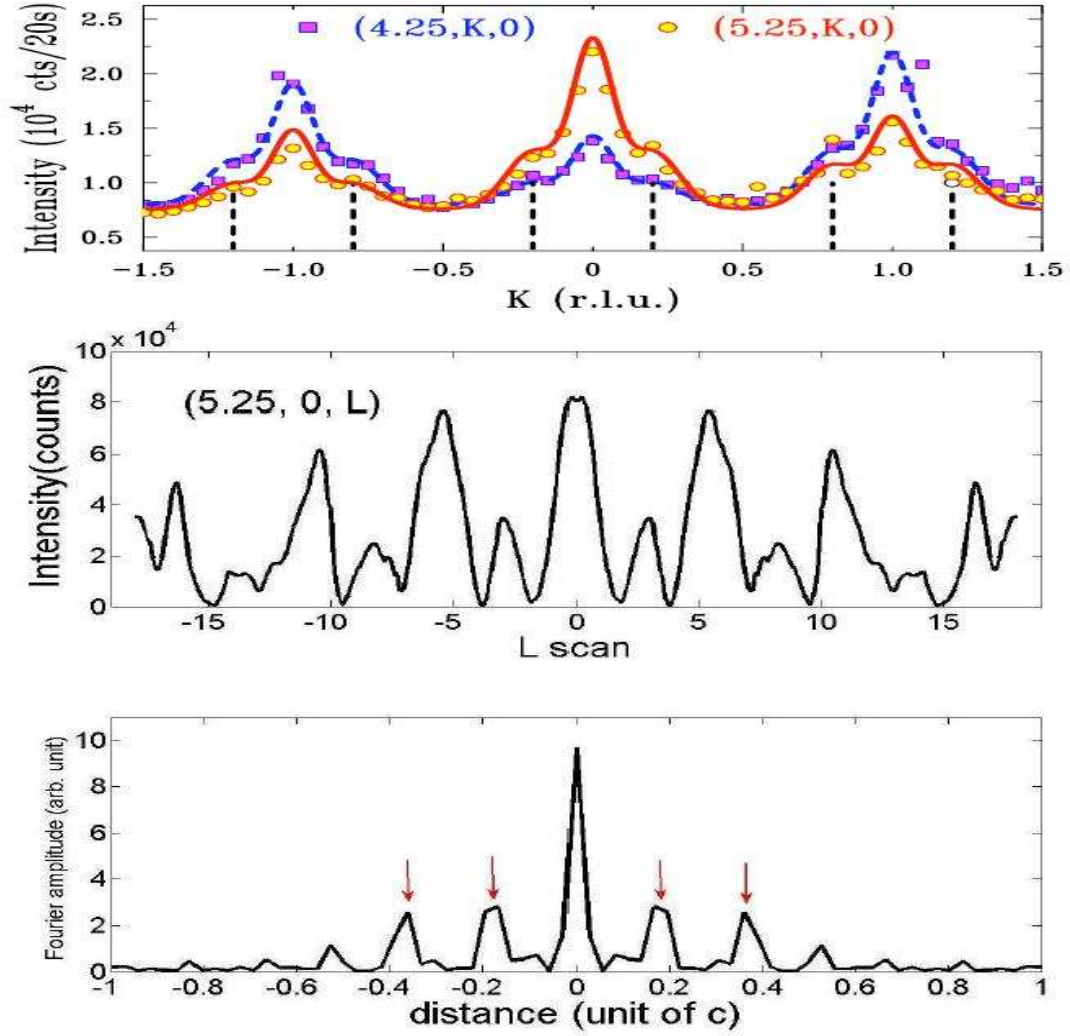


Figure 5.5 Top panel: **K** scans ($T \sim 7K$) across the q_0 satellite peaks. Lines are from Gaussian profile. The vertical dash lines indicate the positions of the shoulders which will be discussed. Middle panel: **L** scan across the $(5.25, 0, 0)$ satellite peak. The data was corrected with geometry correction. Bottom panel: amplitude of the Fourier transformation of the **L** scan. Arrows indicate the main Fourier components.

The broadness of the satellite peaks indicate short range correlation of the $\vec{q}_0$ modulation. From the widths of the satellite peaks along $\mathbf{a}^*$ and $\mathbf{b}^*$ directions, we estimate the correlation lengths to be $\sim 3a$ and $\sim 6b$ along $\mathbf{a}$ and $\mathbf{b}$ directions, respectively, using Scherrer formula[24]. The even broader modulations of the **L**-scan intensity across $(5.25,$

0, 0) satellite peak shown in Fig.(5.5) suggest shorter correlation length along **c** direction. The Fourier transformation of the **L** scan shown in the bottom panel in Fig.(5.5) gives two planar distances along **c** direction, $z_1 \sim 0.18c$ and $z_2 \sim 0.26c$. z_1 corresponds to the distance between CuO₂ and BaO planes and the distance between BaO and CuO chain planes. z_2 corresponds to the distance between CuO₂ and CuO chain planes and the distance between BaO and BaO planes. This agrees well with the ORTHO-IV phase explanation to the satellite peaks: the structure modulations are due to the empty chains in the CuO chain plane and the empty chains introduce lattice modulation to the nearest(BaO) and the second nearest(CuO₂) neighboring planes along **c** direction.

The dominating structure for YBa₂Cu₃CuO_{6.92} is that of the ORTHO-I phase with the CuO chains full. The ORTHO-IV phase due to the ordered clustering of the 8% oxygen vacancies is a minority phase in the crystal. Assuming all the oxygen vacancies participate the ORTHO-IV phase construction, we can estimate the volume ratio of these two structural phases. If denote the volume ratio of ORTHO-IV phase to be x , we have the relation,

$$x * 6.75 + (1 - x) * 7 = 6.92 \quad (5.4)$$

where 6.75 is the oxygen stoichiometry for pure ORTHO-IV phase and 7 is that for ORTHO-I phase. From the above relation, the ORTHO-IV phase is estimated to amount to 30% of the whole sample volume. The actual percentage can be much lower than this value, which is evidenced by the fact that the ORTHO-IV satellite peaks are 6 orders weaker than the average crystal Bragg peaks. The observed ORTHO-IV satellite peaks only suggest that the ORTHO-IV phase is the major form of which the oxygen vacancies are arranged. The oxygen vacancies can certainly be distributed in other ways, ordered or disordered.

This is actually suggested by our X-ray diffuse scattering data which has a large constant background everywhere. From the $\mathbf{K}$ -scan shown in Fig.(5.5), we estimate the ratio of the constant background to the (5.25, 0, 0) satellite peak intensity to be 40%. The large background can be due to other forms of oxygen vacancy distributions which are highly disordered on average.

From the discussion above, we come to the conclusion that majority of the oxygen vacancies in $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ are clustered together to form ORTHO-IV minority phase and the ORTHO-IV type clustering has a very short correlation length. Thus, we believe that the ORTHO-IV minority phase is in the form of small islands embedded in the average crystal rather than forming macroscopic phase separation.

With the presence of ORTHO-IV minority phase islands, the surrounding average lattice is inevitably perturbed and long range strain fields are built up in the crystal. The Huang type diffuse scattering was observed on our sample at low temperature, as shown in the 2-D scans around the (4 0 0) Bragg peak in Fig.(5.6). Fig.5.6(a) shows characteristic

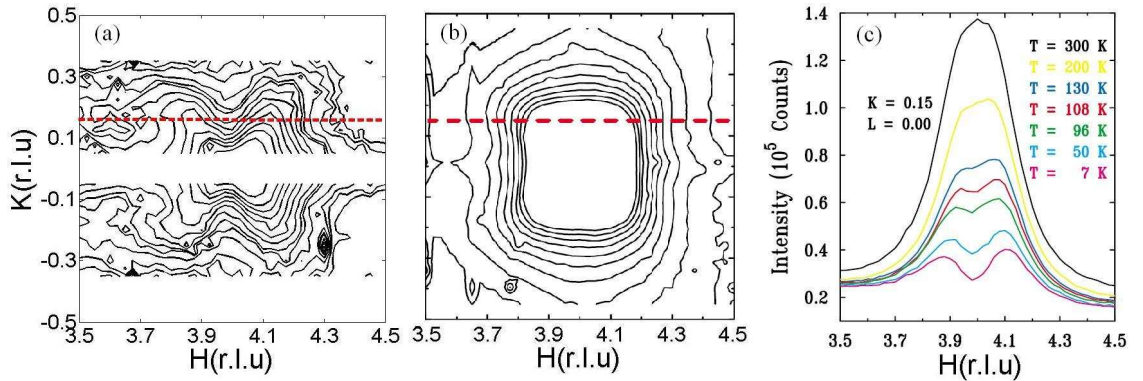


Figure 5.6 (a): contours of the diffuse scattering intensity around (4 0 0) Bragg peak at $\sim 7\text{K}$. Strong HDS dominates the diffuse scattering at this temperature. (b): contours of the diffuse scattering intensity around (4 0 0) Bragg peak at $\sim 300\text{K}$. The main contribution is taken over by TDS. (c): Line scans at different temperatures showing how TDS overwhelms HDS above $\sim 200\text{K}$. Line scans were taken along the dash lines (red) in (a) and (b). See Ref.[7].

HDS pattern at $\sim 7K$ with strong anisotropy in reciprocal space. As temperature increases, the thermal vibration becomes stronger. At $\sim 300K$, the TDS dominates the diffuse scattering intensity with a more isotropic pattern as shown in Fig.5.6(b). The temperature dependent evolution of the overall diffuse scattering intensity away from the satellite peaks is shown more clearly in Fig.5.6(c).

To further characterize the superstructure modulation within the ORTHO-IV minority phase islands, temperature dependent scans were performed across the satellite peaks. The **H** and **K** scans across (5.25, 0, 0) satellite peak as a function of temperature are shown in Fig.(5.7). We notice that the intensity of the (5.25, 0, 0) satellite peak decreases as a

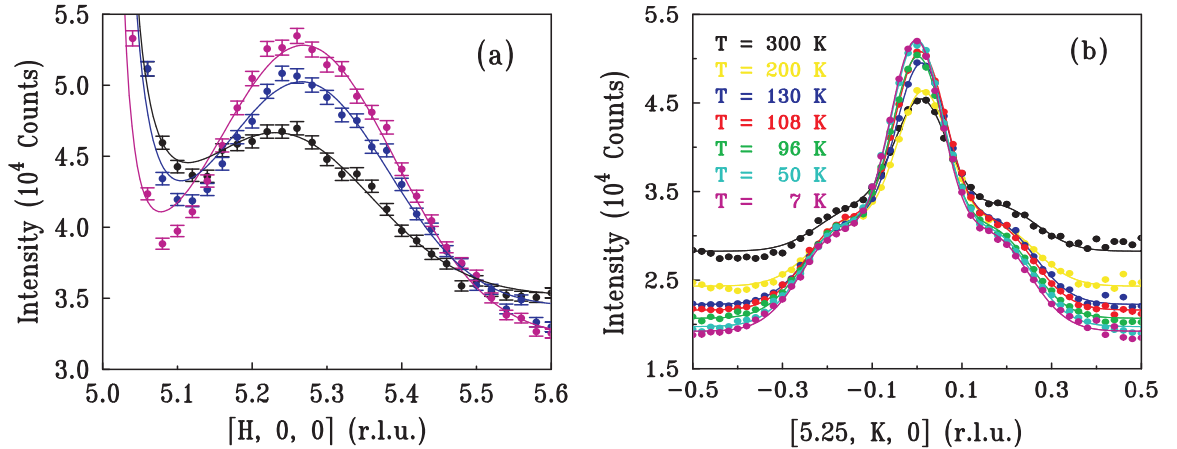


Figure 5.7 Scans across the (5.25, 0, 0) satellite peak at different temperatures[7]. (a): **H**-scans; (b): **K**-scans. The solid lines are fits to Gaussian profile. (a) and (b) share the same color scheme.

function of increasing temperature. In order to get more quantitative information of the satellite peaks as a function of temperature, we fitted the **H** scans with a combination of a Lorentzian(TDS+HDS), a Gaussian(satellite peak) and a constant term(background). The **K** scans were fitted with a combination of three Gaussian and, again, a constant term. The integrated intensities of the (5.25, 0, 0) satellite peak as a function of temperature

are presented in Fig.(5.8). The satellite intensity was also estimated via maximum amplitude of the **L** scan modulation(Fig.(5.5)) defined as $I_{(5.25,0,0)} - I_{(5.25,0,0.18)}$. All three

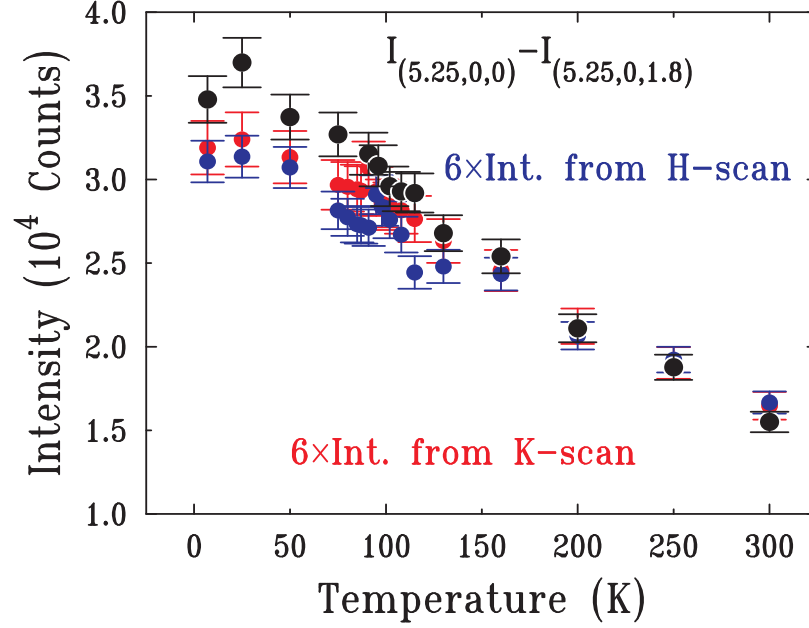


Figure 5.8 Temperature dependence of the (5.25 0 0) peak[7]. The intensity of the peak was extracted in three different ways(see text). All three cases show the temperature dependent behavior consistently.

cases consistently show that the superlattice peak decreases nearly linearly with increasing temperature(Fig.(5.8)). If this linear trend continues, the intensity will extrapolate to zero around $\sim 500K$.

Although the origin of q_0 satellite peaks can be attributed to the ORTHO-IV phase, it is puzzling to observe a large increase of the diffuse satellite peak with decreasing temperature. From $300K$ to $7K$, the intensity of the (5.25, 0, 0) satellite peak increases by $\sim 130\%$. Even though the X-ray scattering intensities generally are expected to increase with decreasing temperature due to the temperature dependence of the Debye-Waller factors(see Eqn.(2.15) for example), the normal Debye-Waller factors of the overall lattice can not account for the observed large increase. Using the Debye-Waller factors measured by

R.P.Sharma *et al.*[75] with neutron diffraction on ceramic $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples, we estimate the X-ray scattering intensities to increase by $\sim 25\%$ when the temperature is decreased from 295K to 10K . The strongest temperature dependent effect is from the Ba ions, of which the modulus square of the Debye-Waller factor is increased by 38% . Thus, the temperature dependence of the Debye-Waller factors is not enough to explain the observed large increase of the satellite intensities.

Since diffusive motion of chain oxygens(O(1)) practically freezes below $\sim 250\text{K}$, the growth of ORTHO-IV phase islands in size or number seems unlikely. The anomalous temperature dependent behavior of the satellite peaks suggests that enhanced elastic softening of the lattice takes place within these regions on lowering temperature. Thus the thermal effect is stronger in the ORTHO-IV phase islands comparing with that of the average lattice, which may account for the 130% increase of the satellite peak intensity when the temperature is lowered from 300K to 7K .

5.3 ORTHO-IV phase modeling and data fitting

In the previous section, we showed that the crystal structure of $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ is intrinsically inhomogeneous at the nano-scale due to the clustering of the oxygen vacancies. Majority of the oxygen vacancies cluster together to form ORTHO-IV phase islands whose dimensions are about several unit cell constants in the **a-b** plane and even shorter along **c** direction. The long range lattice strain built up in the surrounding average lattice due to the ORTHO-IV phase islands is also observed in our X-ray diffuse scattering experiments. Thus the crystal structure of $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ is perturbed at different scales. In this section, we will quantitatively examine these lattice distortions by fitting the observed diffuse scattering

data to an ORTHO-IV phase island model.

5.3.1 Formulation of the diffuse scattering from $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$

As discussed in previous section, in $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$, majority but not all of the oxygen vacancies clusters together to form ORTHO-IV phase islands. The oxygen vacancies distributed in other forms are highly disordered and contribute to the general background to the diffuse scattering. Here we simplify the picture to be radomly distributed ORHO-IV phase islands embedded in average lattice without considering other forms of oxygen vacancy distribution specifically. The diffuse scattering from the ORTHO-IV islands and the associated strain fields and the diffuse scattering due to thermal vibration will be included in our model. Since the TDS does not interfere with the other two types of diffuse scattering, it will be considered separately later and here we concentrate on the scattering from the islands and the associated strain fields. In this case, the X-ray scattering can be generally written as,

$$I(\vec{Q}) = \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot (\vec{R}_{lk} + \vec{u}_{lk} + \vec{v}_{lk})} \right|^2 \quad (5.5)$$

where $\vec{u}_{lk}$ is the superstructure modulation of the ORTHO-IV phase and $\vec{v}_{lk}$ is the strained lattice distortion due to the presence of the ORTHO-IV phase islands as defects. Again, l is the index of unit cells and k is the index of atoms within an unit cell. To separate the diffuse scattering from the Bragg scattering, we rewrite Eqn.(5.5) as,

$$I(\vec{Q}) = \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} + \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} (e^{i\vec{Q} \cdot (\vec{u}_{lk} + \vec{v}_{lk})} - 1) \right|^2 \quad (5.6)$$

The modulus square of the first term gives rise to the Bragg peaks and that of the second term gives the diffuse scattering. The interference of the two terms is sharply centered at the Bragg points and does not contribute to the diffuse scattering. Assuming the $\vec{v}_{lk}$ are small, which is usually the case for long-range strain fields, we expand $e^{i\vec{Q}\cdot\vec{v}_{lk}}$ to the first order. As a result, the diffuse scattering part in Eqn.(5.6) becomes,

$$I_{diff}(\vec{Q}) = \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q}\cdot\vec{R}_{lk}} (e^{i\vec{Q}\cdot\vec{u}_{lk}} - 1) + \sum_{lk} i\vec{Q} \cdot \vec{v}_{lk} \tilde{f}_{lk} e^{i\vec{Q}\cdot\vec{R}_{lk}} e^{i\vec{Q}\cdot\vec{u}_{lk}} \right|^2 \quad (5.7)$$

Assuming the ORTHO-IV islands are randomly distributed without spatial correlation, which is evidenced by the very short range correlation shown by the broadness of the satellite peaks, we ignore the interference of the scattering from different islands. Thus, the diffuse scattering will be the average of the scattering contribution from all the islands and their surrounding distorted lattices. Eqn.(5.7) becomes,

$$I_{diff}(\vec{Q}) = N_0 < \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q}\cdot\vec{R}_{lk}} (e^{i\vec{Q}\cdot\vec{u}_{lk}} - 1) + \sum_{lk} i\vec{Q} \cdot \vec{v}_{lk} \tilde{f}_{lk} e^{i\vec{Q}\cdot\vec{R}_{lk}} e^{i\vec{Q}\cdot\vec{u}_{lk}} \right|^2 > \quad (5.8)$$

where N_0 is the total number of islands and the summation of l is over a single ORTHO-IV island and its surrounding strained lattices. The $e^{i\vec{Q}\cdot\vec{u}_{lk}}$ term is not expanded because the $\vec{u}_{lk}$ are expected to be large from the discussion in the previous section. Thus, the linear approximation is not applicable. In Eqn.(5.8), the modulus square of the first term gives rise to the ORTHO-IV satellite peaks and the modulus square of the second term describes the diffuse scattering from the strained lattice. The interference of these two is also observed in our diffuse scattering experiments which is responsible for the intensity asymmetry about the $\mathbf{K}$ axis through (4, 0, 0) Bragg peak shown in Fig.(5.6). These three contributions to

the overall diffuse scattering intensity will be denoted as I_1 , I_2 and I_3 respectively and they are specifically written down as the following:

$$I_1 = N_0 < \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} (e^{i\vec{Q} \cdot \vec{u}_{lk}} - 1) \right|^2 > \quad (5.9)$$

$$I_2 = N_0 < \left| \sum_{lk} i\vec{Q} \cdot \vec{v}_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} e^{i\vec{Q} \cdot \vec{u}_{lk}} \right|^2 > \quad (5.10)$$

$$I_3 = N_0 < \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} (e^{i\vec{Q} \cdot \vec{u}_{lk}} - 1) \sum_{l'k'} i\vec{Q} \cdot \vec{v}_{l'k'} \tilde{f}_{l'k'} e^{i\vec{Q} \cdot \vec{R}_{l'k'}} e^{i\vec{Q} \cdot \vec{u}_{l'k'}} > + c.c. \quad (5.11)$$

5.3.2 ORTHO-IV phase island modeling

The statistical average in the above equations depends on the details of the oxygen vacancy distribution. From our experimental data, we know that the oxygen vacancies cluster together to form ORTHO-IV phase islands with very short correlation lengths along all directions. However, more detailed information is still missing, which prevent us from further analysis. To overcome this difficulty, a phenomenological model was constructed to describe the ORTHO-IV phase island formation, whose details are given in Appendix A.

Since the ORTHO-IV phase superstructure is of $4a$ periodicity along the **a** direction with one oxygen vacancy in each supercell, we started our modeling by divide the whole crystal into blocks which contain $4 \times 1 \times 1$ unit cells along **a**, **b** and **c** directions. We use $\langle s(m) \rangle$ to describe the probability of the m -th block containing an oxygen vacancy and $c(m, n)$ to describe the paring correlation function of the oxygen vacancy distribution in the m -th and n -th blocks. The details of functions $\langle s(m) \rangle$ and $c(m, n)$ can be found in Appendix A. Based

on our model, the statistical average was carried out and Eqn.(5.9,5.10,5.11) become,

$$I_1 = N_0 \left| \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \right|^2 \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} \langle s(m) \rangle \langle s(m') \rangle c(m, m') \quad (5.12)$$

$$I_2 = N_0 \left| \frac{1}{M} \sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} \sum_{\alpha\beta\gamma} Q_\alpha \mathbb{D}_{\alpha\beta}^{-1} \bar{p}_{\beta\gamma} q_\gamma \right|^2 \quad (5.13)$$

$$I_3 = -\frac{N_0}{M} \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \sum_m e^{i\vec{Q} \cdot \vec{R}_m} \langle s(m) \rangle \sum_{k'} \tilde{f}_{k'} e^{i\vec{G} \cdot \vec{R}_{k'}} \sum_{\alpha\beta\gamma} Q_\alpha \mathbb{D}_{\alpha\beta}^{-1} \bar{p}_{\beta\gamma} q_\gamma + c.c. \quad (5.14)$$

where m and m' are the indexes of the blocks and h is the index of unit cells within one block. k and k' are used to index the atoms within an unit cell as usual. $\vec{u}_{hk}^0$ present the average distortion pattern of the ORTHO-IV phase supercells. M is the mass of an unit cell.

As to the strain, M.A.Krivoglaz[35] and P.H.Dederichs[34] suggested that, for very loose defect clusters, the displacement fields associated with individual defects can still be described by Eqn.(3.35) in terms of Kanzaki forces and they simply superimpose on each other. During our model construction, we noticed that this treatment broke down for the strain fields induced by ORTHO-IV phase islands in $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$. In practice, we treated the ORTHO-IV island as a whole “big” defect and introduced a *empirical* force dipole matrix to describe the associated strain fields. To distinguish it from the P matrix in Eqn.(3.39) which is very well physically defined, we use the notation $\bar{p}$ here.

5.3.3 Fitting the ORTHO-IV phase modulation pattern

In order to understand the observed diffuse scattering from $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$, a “zero”-th order model has been constructed with more than twenty parameters. In principle, a point-to-point fitting of the observed diffuse scattering data of a very large reciprocal space range is needed to resolve so many parameters. This scheme is impractical because of the huge amount of computation required. Fortunately, the four major contributions to the overall diffuse scattering intensity, namely the ORTHO-IV phase satellites, the HDS, the interference of the scattering from the ORTHO-IV phase island and its surrounding strained lattice and the TDS, each have their own characteristics and dominate different regions in reciprocal space. This allows us to decouple most of the parameters and fit them separately with reasonable accuracy.

The scattering from the ORTHO-IV phase island, I_1 , is the easiest one to be separated from the other contributions because it gives rise to the characteristic $\vec{G} \pm \vec{q}_0$ peaks. The satellite peaks dominate the diffuse scattering intensities near the $\vec{G} \pm \vec{q}_0$ regions, which can be seen from Fig.(5.4) and Fig.(5.5). Close to the satellite peaks, the other contributions are much weaker and vary slowly as a function of $\vec{q}$. Since the satellite peaks are sharper than TDS and HDS and they are located away from the Bragg peaks, we extract the intensity of the scattering from the ORTHO-IV phase islands by fitting the $\mathbf{K}$ scans through $\vec{G} \pm \vec{q}_0$ with three Gaussian and a constant term, as shown in Fig.(5.5) and Fig.(5.7). This satellite peak intensity extraction scheme will of course involve errors, depending on how well the “background” can be modeled by two Gaussians and a constant. Later we will show full two dimensional diffuse scattering intensity simulation based on the determined parameters around the (4, 0, 0) and (5, 0, 0) Bragg peaks, which shows good agreement

with the experimental observation.

Since the oxygen empty chains are 1-D objects running along the **b** direction as shown in Fig.(A.1), the distortion vectors, $\vec{u}_{hk}^0$ in Eqn.(5.12), are expected to be in the **ac** plane. The displacements along **a** and **c** directions can be decoupled by choosing the satellite peaks whose $\vec{Q}$ vectors have no **c*** components ($\vec{Q} = (m, n, 0) \pm (\frac{1}{4}, 0, 0)$ with m and n to be integers, for example). From Eqn.(5.12), we can see that the **c** direction components of $\vec{u}_{hk}^0$ have no effect on I_1 if $\vec{Q}$ is confined within **a*****b*** plane as described above. In the following discussion, we will denote the three components of $\vec{u}_{hk}^0$ along **a**, **b** and **c** directions as u_{hk}^{0a} , u_{hk}^{0b} and u_{hk}^{0c} , respectively. Within a 4x1x1 ORTHO-IV phase supercell, there are totally 51 atoms. Thus there are 51 u_{hk}^{0a} along **a** directions in principle. This number can be drastically reduced based on the following symmetry consideration.

The projection of the arrangement of the atoms within a 4x1x1 ORTHO-IV phase supercell on the **a-c** plane is shown in Fig.(5.9) without assigning the superstructure modulation. It is obvious that the other parts of the whole supercell are related to the shaded area with mirror symmetry. Thus the u_{hk}^{0a} of individual ions are not totally independent of each other. For example, if we denote the u_{hk}^{0a} of the two Ba ions as (δ_1, δ_2) from left to right in the shaded area, the u_{hk}^{0a} for all the Ba ions within the supercell would be,

$$\begin{pmatrix} \delta_1 & \delta_2 & -\delta_2 - \delta_1 \\ \delta_1 & \delta_2 & -\delta_2 - \delta_1 \end{pmatrix}$$

due to the mirror symmetry. Also, the ions on the left and right edges of the shaded area, which are emphasized by the two black rectangles, are located in the mirror planes of the ORTHO-IV phase superstructure. Thus, the u_{hk}^{0a} of those ions are zero. Further, from

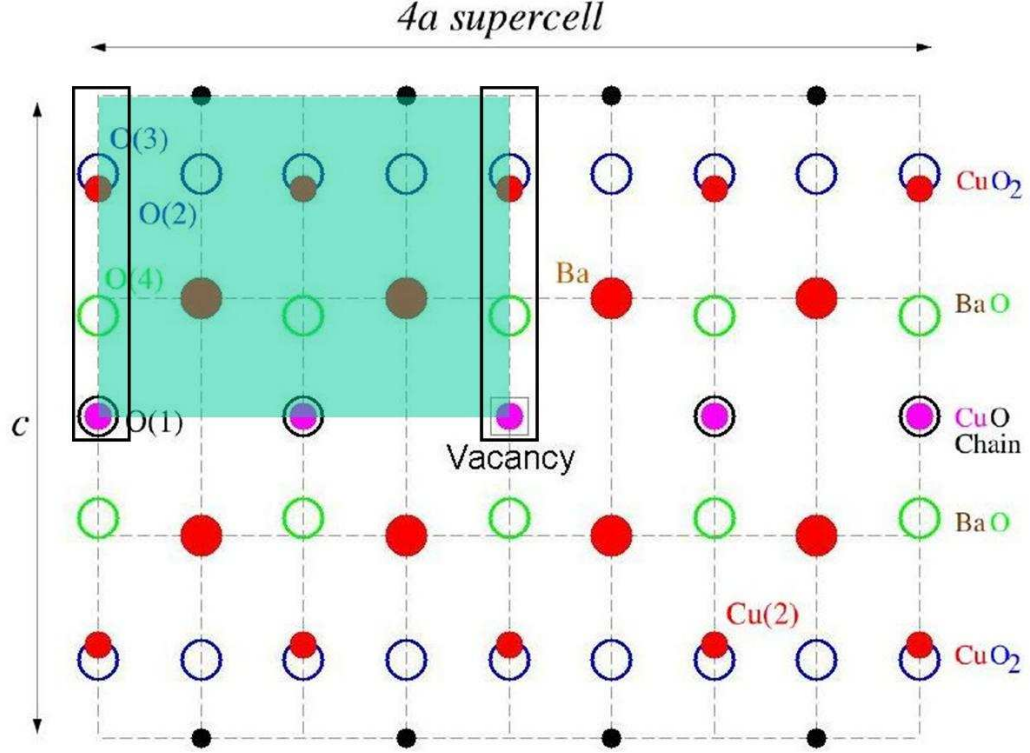


Figure 5.9 projection of the arrangement of the atoms within a $4 \times 1 \times 1$ ORTHO-IV phase supercell on the a - c plane without assigning the superstructure modulation. The other parts of the supercell are related to the shaded area with mirror symmetry. The rectangles indicate the atoms located in the mirror planes.

analysis of the $\mathbf{L}$ scan through the $(5.25 \ 0 \ 0)$ satellite peak given in previous section, we know that the satellite gets contributions mainly from the scattering from the chain planes, the BaO planes and the CuO₂ planes. The contribution from the scattering from the Y planes is much smaller if there is any. So, we assume the u_{hk}^{0a} of the Y ions are zero in our fitting. Thus, the $\{u_{hk}^{0a}\}$ for the whole supercell becomes a parameter group with 9 elements: two for O(2), one for O(3), one for Cu(2), two for Ba, one for O(4), one for O(1) and one for Cu(1).

$\mathbf{K}$ scans through 45 satellite peaks with $\vec{Q} = (m, n, 0) \pm (\frac{1}{4}, 0, 0)$ (m and n are integers) were collected to fit the ORTHO-IV phase superstructure modulation pattern $\vec{u}_{hk}^0$ along $\mathbf{a}$ direction, namely the 9 elements of $\{u_{hk}^{0a}\}$. In order to do the line fitting to the

Gaussian profiles of the satellite peak intensities extracted with the scheme discussed above, we need to consider the average island shape function $\langle s(m) \rangle$ and the oxygen vacancy paring correlation function $c(m, n)$ specifically as formulated in Eqn.(5.12). These two functions will add six more parameters to the fitting procedure, namely the island half widths (w_a, w_b) , (d_a, d_b) governing the slopes of the average island edges and the oxygen vacancy correlation lengths (ξ_a, ξ_b) as defined in previous section. The fitting is still complicated and involves heavy computation. We will further simplify the fitting procedure by examining Eqn.(5.12).

We notice that the second summation in Eqn.(5.12),

$$\sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} \langle s(m) \rangle \langle s(m') \rangle c(m, m')$$

is translationally invariant in reciprocal space if $\vec{Q}$ is changed by $\Delta\vec{Q}$ where $\Delta\vec{Q} = (\frac{n_1}{4}, n_2, 0)$ (n_1 and n_2 are integers). From the definition of $\vec{R}_m$, we know that $\vec{R}_m - \vec{R}_{m'} = (4n_3a, n_4b, 0)$ (n_3 and n_4 are integers). As a result, $e^{i\Delta\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} = e^{i2\pi(n_1n_3 + n_2n_4)} \equiv 1$. Thus, this term is the same for all satellite peaks which gives the characteristic peak profile for the ORTHO-IV phase satellites. Compared with it, the first summation, which governs the height(or strength) of the satellite peaks, is varying much more slowly as a function of $\vec{Q}$. By fitting the **K** scans shown in Fig.(5.5) with Gaussians, we estimate the Full Width Half Maximum(FWHM) of the satellite peaks to be $0.14 \frac{2\pi}{b}$ on the average. For a Gaussian profile, a integration in the range of $0.85 * [-FWHM, FWHM]$ amounts to more than 95% of the full value. Thus, a integration of the individual satellite peaks along **K** direction in the range of $\vec{G} + \vec{q}_0 \pm (0, 0.12, 0)$ should give very good accuracy. Since the first summation is varying slowly as a function of $\vec{Q}$, we assume it is a constant within this small $\vec{Q}$ range

and write the integration of I_1 along $\mathbf{K}$ direction as,

$$\begin{aligned}
& N_0 \int_{\vec{Q}_0 - \delta\vec{Q}}^{\vec{Q}_0 + \delta\vec{Q}} \left| \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \right|^2 \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} \langle s(m) \rangle \langle s(m') \rangle c(m, m') dK \\
& \approx N_0 \left| \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q}_0 \cdot \vec{R}_{hk}} (e^{i\vec{Q}_0 \cdot \vec{u}_{hk}^0} - 1) \right|^2 \int_{\vec{Q}_0 - \delta\vec{Q}}^{\vec{Q}_0 + \delta\vec{Q}} \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} \langle s(m) \rangle \langle s(m') \rangle c(m, m') dK
\end{aligned}$$

where $\vec{Q}_0 = \vec{G} \pm \vec{q}_0$ and $\delta\vec{Q} = (0, 0.12, 0)$. Since the integration over the second summation is the same for all the $\vec{Q}_0$ values as discussed above, the integrated intensities of the satellite peaks are approximately proportional to modulus square of the supercell structure factors $|\sum_{hk} \tilde{f}_{hk} e^{i\vec{Q}_0 \cdot \vec{R}_{hk}} (e^{i\vec{Q}_0 \cdot \vec{u}_{hk}^0} - 1)|^2$. Thus, we can fit the integrated satellite peak intensities with the 9 elements of $\{u_{hk}^{0a}\}$ and a scaling factor, without considering the parameters in function $\langle s(m) \rangle$ and $c(m, m')$ at the moment. The determined u_{hk}^{0a} from fitting to the measured 45 satellite peaks are shown in Fig.(5.11). In Fig.(5.4), we show the comparison of the integrated satellite intensities (black vertical lines) with the calculated $|\sum_{hk} \tilde{f}_{hk} e^{i\vec{Q}_0 \cdot \vec{R}_{hk}} (e^{i\vec{Q}_0 \cdot \vec{u}_{hk}^0} - 1)|^2$ (red vertical lines) for some of the measured satellite peaks.

In our “zero”-th order ORTHO-IV phase model, we assume the island height in the $\mathbf{c}$ direction is one unit cell in length. Thus, the $\mathbf{c}$ direction component of $\vec{R}_m$ is zero and the second summation in Eqn.(A.7) does not depend on the $\mathbf{c}^*$ direction component of $\vec{Q}$. As a result, for the $\mathbf{L}$ scan shown in Fig.(5.5), the second summation is a constant. We only need to fit the whole curve to the modulus square of the supercell structure factor $|\sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1)|^2$ with a set of u_{hk}^{0c} , together with the determined parameters $\{u_{hk}^{0a}\}$. Totally 13 elements of $\{u_{hk}^{0a}\}$ are assigned to the ions within a supercell based on the same symmetry argument for the $\mathbf{a}$ direction displacement pattern discussed before: 3 for

O(4), 2 for Ba, 3 for O(3), 2 for O(2) and 3 for Cu(2) respectively. The determined u_{hk}^{0c} from fitting are also shown in Fig.(5.10). The comparison of the measured **L** scan(background and absorption corrected) with the calculated curve based on the determined supercell displacement pattern is shown in Fig.(5.11).

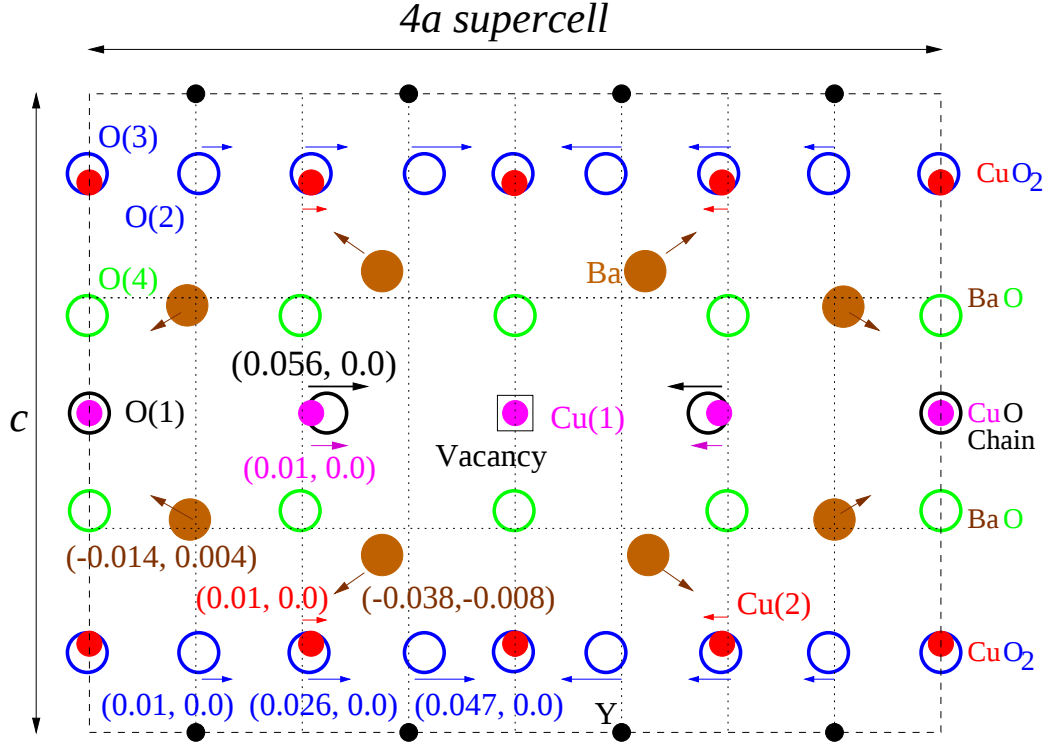


Figure 5.10 The fitted atomic displacement(arrows) pattern at $\sim 7K$ [7]. All the atoms have been projected on the ac plane. Note that primary displacements $\vec{u}_{hk}^0$ are along the a axis, *i.e.*, along the shorter Cu-Cu bond direction. $(u_{hk}^{0a}, u_{hk}^{0c})$ of respective atoms are given in parentheses in units of lattice constants a and c . $\vec{u}_{hk}^0$ of all the other atoms are related by mirror symmetry as discussed.

Even though totally 22 elements of $\{u_{hk}^{0a}\}$ and $\{u_{hk}^{0c}\}$ were assigned to the atoms as parameters in our fitting, the fitting procedure is not equally sensitive to all of them. The contribution to the diffuse scattering intensity from an individual atom is not only depends on the amplitude of displacement of that atom but also depends on its scattering factor. With the incident photon energy to be $36Kev$ in our experiments, the scattering

factors, f_O , f_{Cu} and f_{Ba} , are 1.9, 11.5 and 26.4 respectively at $\vec{Q} = (5.25, 0, 0)$ (the values are from the International tables[26]). Thus, the scattering from Ba and Cu, especially the Ba, dominate the diffuse scattering intensities and our analysis is not sensitive to some of the parameters. As a result, 13 out of 22 parameters are determined from our fitting with reasonable accuracy and they are shown in Fig.(5.10). The other 9 were kept to be zero since practically, by tuning their values around, the effect on the calculated diffuse scattering intensity is negligible.

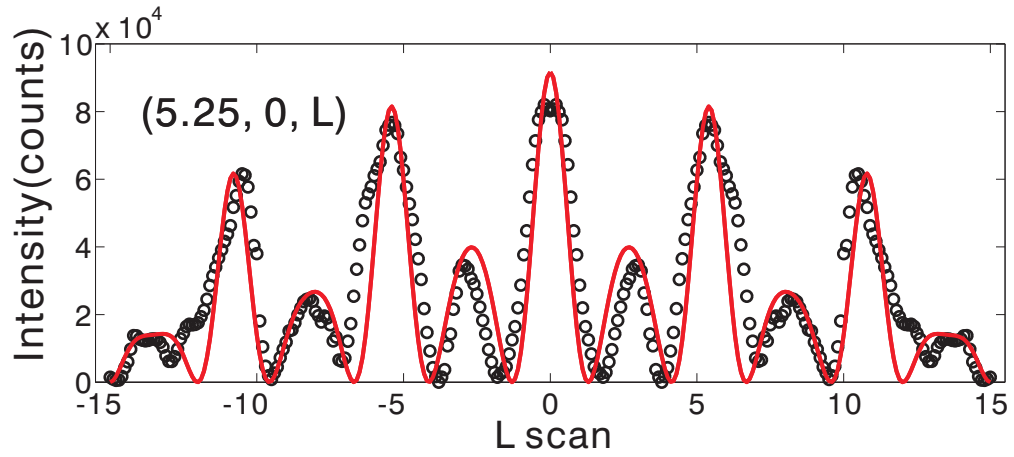


Figure 5.11 Comparison of the measured (5.25 0 L) scan (black circle) with the calculated curve (red line) based on the determined supercell displacement pattern shown in Fig.(5.10). The L scan was corrected with background subtraction and absorption correction.

With the fitted ORTHO-IV phase superstructure modulation pattern presented in Fig.(5.10), the integrated satellite peaks intensities and the long range $\mathbf{L}$ scan crossing (5.25, 0, 0) satellite peak can be reproduced reasonably well, which has been shown in Fig.(5.4) and Fig.(5.10). While the model obtained may not be perfect since many assumptions and simplifications have been made during our model construction, it does account for all the systematics of the experimental data. Further more, it portrays a pattern of displacements similar to that of ORTHO-V phase in an underdoped YBCO obtained from first-principles

electronic calculations by D. de Fontaine *et al.*[67], which was published after our fitting had been done. For example, the Ba ions are moving away from the oxygen vacancies and the displacements are mainly along **a** direction. Of course the theoretical calculation is for ORTHO-V phase with a $\langle 10110 \rangle$ oxygen vacancy pattern while in our case it is ORTHO-IV phase. Still, the similarity of the two displacements patterns, one from a theoretical calculation and the other from purely experimental data fitting, provides further support to our fitting results.

Our X-ray diffuse scattering experiments on $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ show the existence of ORTHO-IV minority phase islands embedded in the average lattice due to oxygen vacancy clustering. The most remarkable feature revealed by our modeling of ORTHO-IV phase superstructure modulation is the correlated atomic displacements of Ba, Cu and O atoms respectively. The CuO_2 planes, where the superconductivity is believed to originate, are heavily involved in the structural modulation to give rise to the observed X-ray scattering pattern. This structural modulation inevitably perturbs the electronic properties associated with the CuO_2 planes and leaves the system to be intrinsically inhomogeneous, both structurally and electronically.

Our fitting results indicate that the structural modulations are fairly strong. In Fig.(5.10), we show that largest u_{hk}^{0a} for Ba, Cu(1), Cu(2), O(2) and O(3) are 0.038, 0.056, 0.01, 0.026 and 0.047 in units of the lattice constant a , which are 0.1449, 0.2135, 0.0381, 0.0991 and 0.1792 in units of angstroms, respectively. These displacements are large and the criteria, $\vec{Q} \cdot \vec{u}_{hk}^0 \ll 1$, to make linear approximation for $e^{i\vec{Q} \cdot \vec{u}_{hk}^0}$ breaks down at, for example, $\vec{Q} = (5.25, 0, 0)$. To further appreciate how strong the lattice modulations are, we compare u_{hk}^{0a} with the standard deviations of the ion positions due to thermal vibration. Based on

the thermal vibration parameters measured by R.P.Sharma *et al.*[75] on optimally doped YBCO, the the standard deviations of the ion positions due to thermal vibration at 295K for Ba, Cu(1), Cu(2), O(2) and O(3) are calculated to be 0.0785, 0.0685, 0.0616, 0.0780 and 0.0780 in units of angstroms. Comparing with these values, u_{hk}^{0a} due to lattice modulations are generally two to three times larger.

S.Agrestini and co-workers have examined[76] the relation between the Cu(2)-O(2,3) bond length with the maximum superconducting transition temperature T_c for different cuprate families. The showed that, from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ to $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$, the Cu-O distance changes from 1.88Å to 1.92Å. Within the 0.04Å variation, the T_c increases by about 100K. Thus, with the large displacements and the direct involvement of the CuO_2 planes, the lattice modulations within the ORTHO-IV phase island due to oxygen vacancy ordering in $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ can perturb the local electronic structures significantly and may have profound and fundamental influence on the global superconductivity properties of this compound.

5.4 Thermal diffuse scattering subtraction

In chapter 2, we introduced Eqn.(2.20) to calculate the thermal diffuse scattering(TDS) at low temperature when the phonon population for high energy optical modes are very small and can be ignored. With the measured elastic constants available in literature, the TDS can be calculated with Eqn.(2.20) to a scaling constant comparing with experimental data which needs to be determined from fitting.

It turns out that this constant can be determined in another way rather than fitting the overall diffuse scattering intensity at low temperature involving all the other

diffuse scattering contributions. The shell model[77, 27] has been commonly used to reconstruct the whole phonon dispersion spectrum, including the optical modes, for ionic materials based on the experimentally measured phonon dispersion curves. S.L.Chaplot *et al.* have shown[78] that the ionic shell model is able to describe very satisfactorily the phonon dispersion relations of the cuprates. Once the whole phonon dispersion spectrum is reconstructed with the shell model, in principle, the TDS, including the contributions from the optical-type lattice vibrations, can be calculated in a large temperature range including high temperature regime where the acoustic approximation breaks down. In Fig.(5.6), we have shown that the TDS overwhelms the HDS above $\sim 200K$ and dominates the diffuse scattering at room temperature. Thus, we can fit the diffuse scattering intensities away from the ORTHO-IV phase satellite peak region at room temperature to determine the scaling factor, assuming the diffuse scattering is due to TDS only. Professor Robert McQueeney at Iowa State University helped us to calculate the TDS in the $7K$ to $300K$ temperature range based on the phonon dispersion relations reconstructed with the shell model. The parameters for the shell model were determined by fitting to the measured phonon dispersion curves[78]. The fitting of the calculated TDS to experimental data at $T = 300K$ is shown in Fig.(5.12). The scan is along $\mathbf{a}^*$ direction through $(4, 0.15, 0)$, same as the red lines in Fig.(5.6). The experimental data shows some extra intensities on the shoulders comparing with the calculated TDS. The green dash line is the difference of the two, which remarkably resembles the low temperature scans shown in Fig.(5.6) when the HDS dominates. Thus it is conceivable that it is the remnant HDS which is much weaker comparing with TDS at room temperature and has been ignored in the fitting.

With the scaling constant determined, we were able to calculate the TDS at low

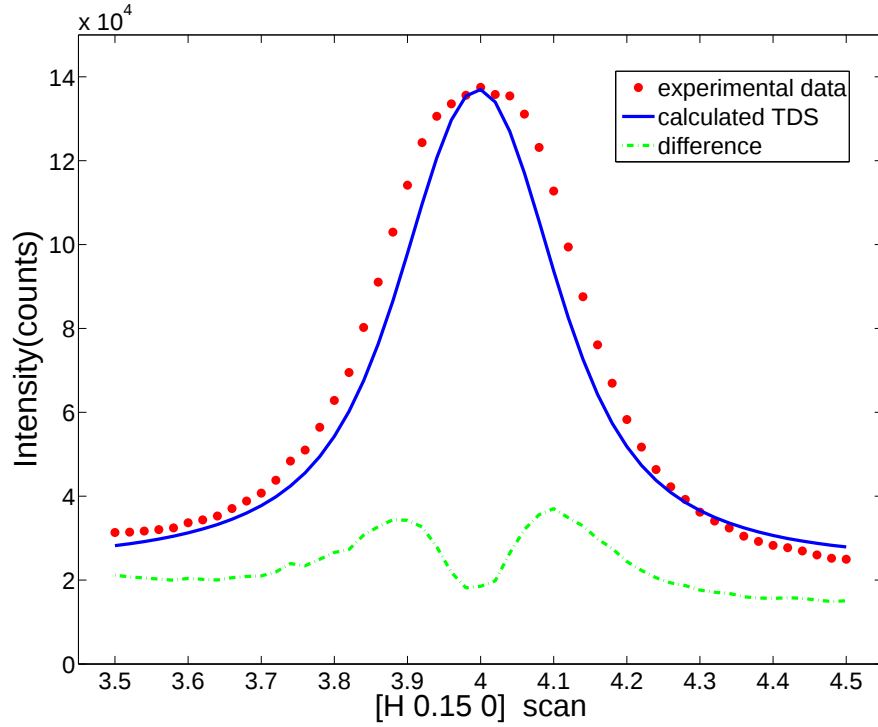


Figure 5.12 fitting of the 300K [H 0.15 0] scan with TDS calculated based on the shell model to determine the scaling constant. Red dot: experimental data; blue curve: calculated TDS; green dash line: the difference between the two. The green dash line resembles the same H scan at 7K as shown in Fig.(5.6).

temperature and subtract it from the overall diffuse scattering intensities. This greatly improved the accuracy of the other parameters from fitting. From here on, all the data presented will be TDS subtracted unless specifically mentioned otherwise.

5.5 Fermi-surface-induced lattice modulation

With the ORTHO-IV phase superstructure modulation pattern obtained, we attempted to fit the 2-D diffuse scattering data collected around (4, 0, 0) and (5, 0, 0) Bragg peaks(Fig.(5.13a)) to extract information about the ORTHO-IV minority phase islands induced lattice strains. In Fig.(5.13a), the scattering intensities due to HDS and the

ORTHO-IV minority phase islands can be clearly identified. The intensity asymmetry about the $\mathbf{K}$ axis through $(4, 0, 0)$ is due to the interference scattering (IFS) from the ORTHO-IV phase islands and the surrounding lattice-strain fields, as formulated in Eqn.(5.14). Except for these pronounced features, detailed quantitative analysis to our diffuse scattering data reveals the existence of a $\mathbf{b}$ direction lattice modulation which was not expected when the experiments were performed. In this section, we will discuss the fitting of the 2-D diffuse scattering pattern and the $\mathbf{b}$ direction lattice modulation.

5.5.1 $\mathbf{b}$ direction lattice modulation revealed by fitting

The salient feature in Fig.(5.13a) is the profound difference in the symmetry of scattering around the two Bragg peaks. While the dominating feature around the $(4, 0, 0)$ Bragg peak is a strong nearly fourfold ‘bow-tie’-shape HDS pattern albeit asymmetric, it is entirely missing around $(5, 0, 0)$. Rather, there is a strong ‘elliptical’ pattern centered at the $(5.25, 0, 0)$. The intensity near $(3.50, 0, 0)$ is from the tail of the strong $\mathbf{q}_0$ -satellite at $(3.25, 0, 0)$. We further notice that there exist subtle but clear shoulders on both sides of the satellite peaks in the $\mathbf{K}$ scans, as shown in Fig.(5.5)(indicated with vertical dash bars) and Fig.(5.13b,5.13c).

The diffuse scattering pattern around $(4, 0, 0)$ shown in Fig.(5.13a) suggests that the shoulders of $(4.25, 0, 0)$ satellite peak in Fig.(5.13b) might be due to the lobes of HDS, extending roughly along $[1\ 1\ 0]$ directions. But this scenario is unlikely to account for the strong shoulders of the $(5.25, 0, 0)$ satellite in Fig.(5.13c) given the absence of similar HDS around $(5, 0, 0)$ Bragg peak.

The absence of HDS around $(5, 0, 0)$ can be understood by examining the general nature of HDS. Even though we have claimed that the HDS from $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ is

too complicated to be deduced from a microscopic picture and we will use the *empirical* equation(A.13) in our fitting, one property of the HDS is certain: as a long-range elastic distortion of which the atoms within an unit cell are displaced in the same way, the strain fields give rise to HDS in the vicinity of a given Bragg point in proportion to the square of the unit cell structure factor modulus(the first summation in Eqn.(A.13)), $|F(\mathbf{G})|^2 = |\sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k}|^2$, where $\vec{G}$ is the Bragg point[34, 79, 35]. For $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$, $|\frac{F([500])}{F([400])}|^2 \approx 0.02$. Using this ratio and the known intensity near (5.25, 0, 0) we estimate the HDS and IFS terms together to account for less than 5% of the intensity of the shoulders of the (5.25, 0, 0) satellite peak. This is clearly illustrated in Fig.(5.13c) where we show the $\mathbf{K}$ scan through (5.25, 0, 0) satellite peak together with that through (4.25, 0, 0) but scaled down by a factor of 5(this value is still much greater than the ~ 0.02 ratio we estimated). The HDS is too weak to account for the the shoulders of the (5.25, 0, 0) satellite peak. Thus, the shoulders must be the finger print of a lattice modulation along the $\mathbf{b}$ axis. In the following discussion, the shoulders will be denoted as $\vec{G} \pm \vec{q}_0 \pm \vec{q}_1$ where $\vec{G} \pm \vec{q}_0$ has been used to denote the ORTHO-IV satellite peaks in previous discussion.

In Fig.(5.14), we show the $\mathbf{H}$ scan through the shoulder of (5.25, 0, 0) satellite peak. The vertical red dash line indicates that the shoulder also peaks at $\mathbf{H}=5.25$, suggesting the centers of the shoulders have the same $\mathbf{a}^*$ component as that of the satellite peaks. Thus, $\vec{q}_1$ does not carry further $\mathbf{a}^*$ component and it can be written as (0, δ , 0) with δ to be determined. Since the shoulder structure is on top of the strong and broad ORTHO-IV phase satellite peaks, one can argue that the scan shown in Fig.(5.14) may not conclusively prove that the centers of the shoulders have the same $\mathbf{a}^*$ component as that of the satellite peaks. However, the following discussion will show that the shoulders are closely related to

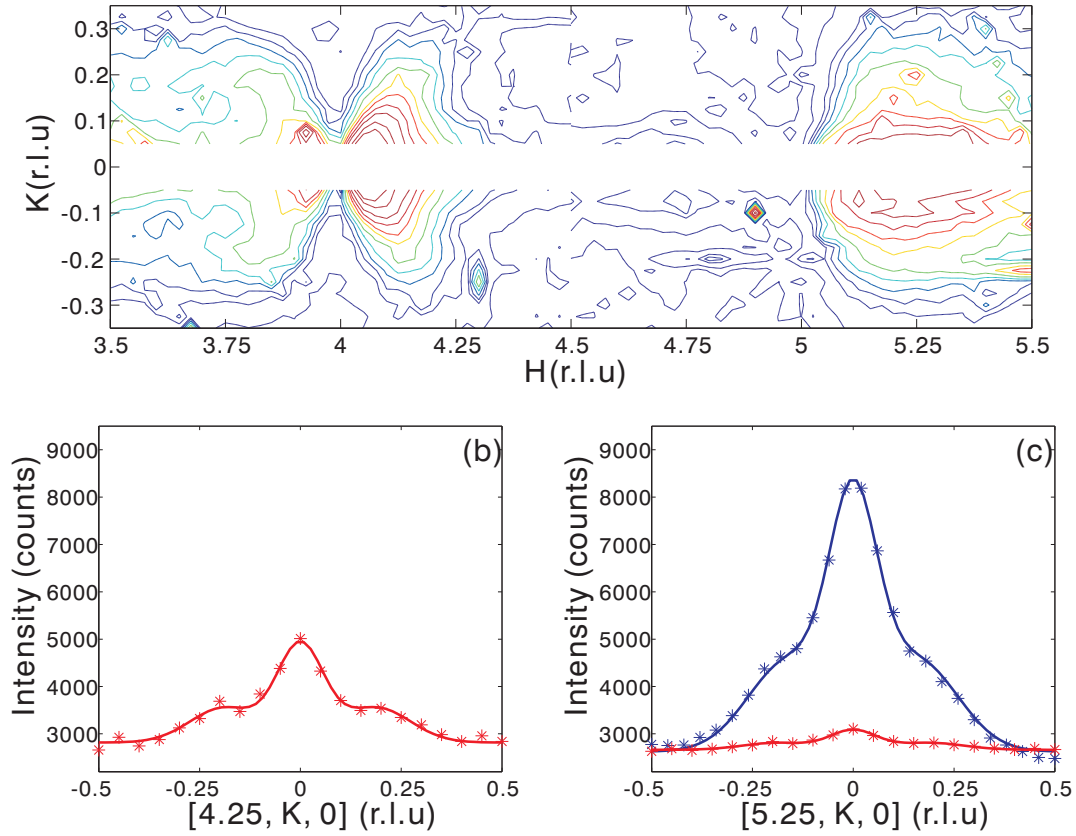


Figure 5.13 (a): the 2-D diffuse scattering pattern in a^*-b^* plane around (4 0 0) and (5 0 0) Bragg peaks. (b): the $\mathbf{K}$ scan through (4.25, 0, 0) satellite peak. (c): $\mathbf{K}$ scan through (5.25, 0, 0) satellite peak (blue) together with that through (4.25, 0, 0) (red) but scaled down by a factor of 5.

the center satellite peaks.

To further explore the origin of the shoulders, the $\mathbf{K}$ scans through different $\mathbf{q}_0$ peaks need to be examined more closely. In Fig.(5.5), long $\mathbf{K}$ scans through several $\mathbf{q}_0$ peaks are shown. It is interesting to notice that $\mathbf{K}$ -scans through different $\mathbf{q}_0$ peaks show a definite correlation between the intensities of the shoulder peaks with the center ORTHO-IV peaks, both having roughly the same correlation lengths and obeying the same parity relations(see discussion in section(4.2)). Wherever the satellite peaks are stronger, the shoulders are stronger and vice versa. The parity relations impose stringent phase correlations between

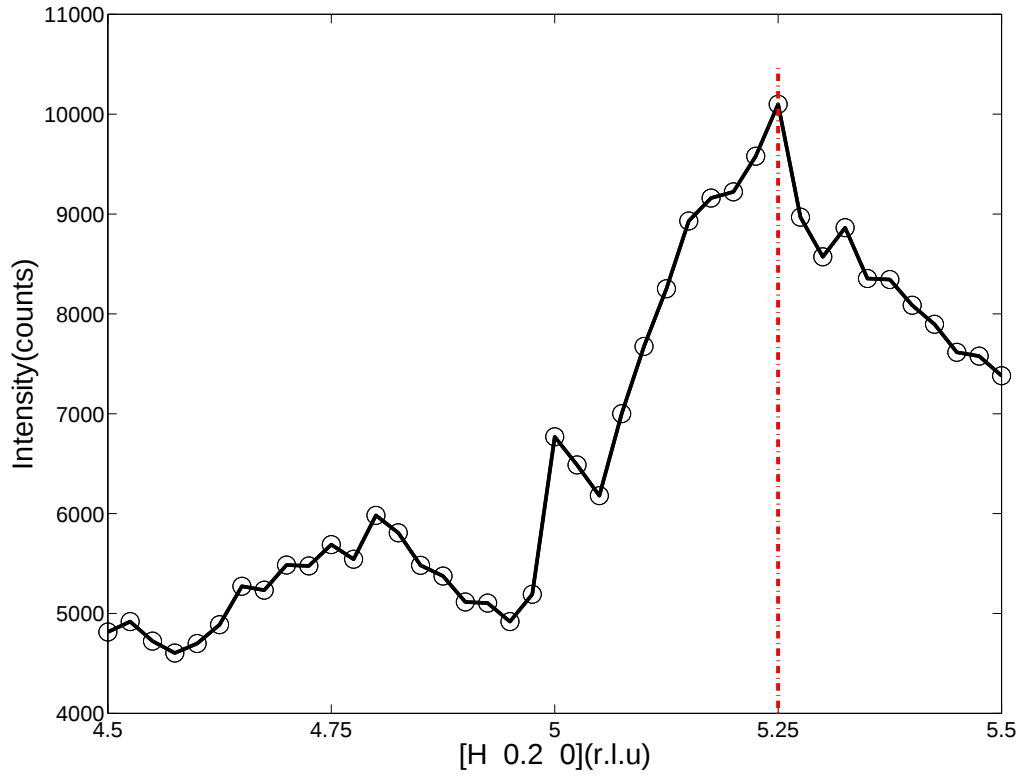


Figure 5.14 H scan through the shoulder of $(5.25, 0, 0)$ satellite peak. Red dash line is at $H=5.25$.

atomic displacements such as those in the fitted ORTHO-IV model. Furthermore, careful measurements of the ratio between the $(5.25, 0, 0)$ satellite and the $(5.25, 0, 0) \pm \vec{q}_1$ shoulder intensities as a function of increasing temperature found it to be constant in the range of 7-300K (Fig.(5.15)). The intensities are extracted by fitting the $\mathbf{K}$ scans with three Gaussian. As pointed out before (see Fig.(5.8) and the discussion in section(4.2)), the temperature dependence of the $\mathbf{q}_0$ peaks distinguishes the ORTHO-IV phase islands from the average lattice which has less rapidly varying Debye-Waller factors. The fact that the intensities of the shoulders obey the same temperature dependence as the center $\mathbf{q}_0$ peak strongly indicates that they are intimately related. Therefore, the $\mathbf{q}_1$ modulation must coexist with

ORTHO-IV islands and does not form homogeneously throughout the crystal.

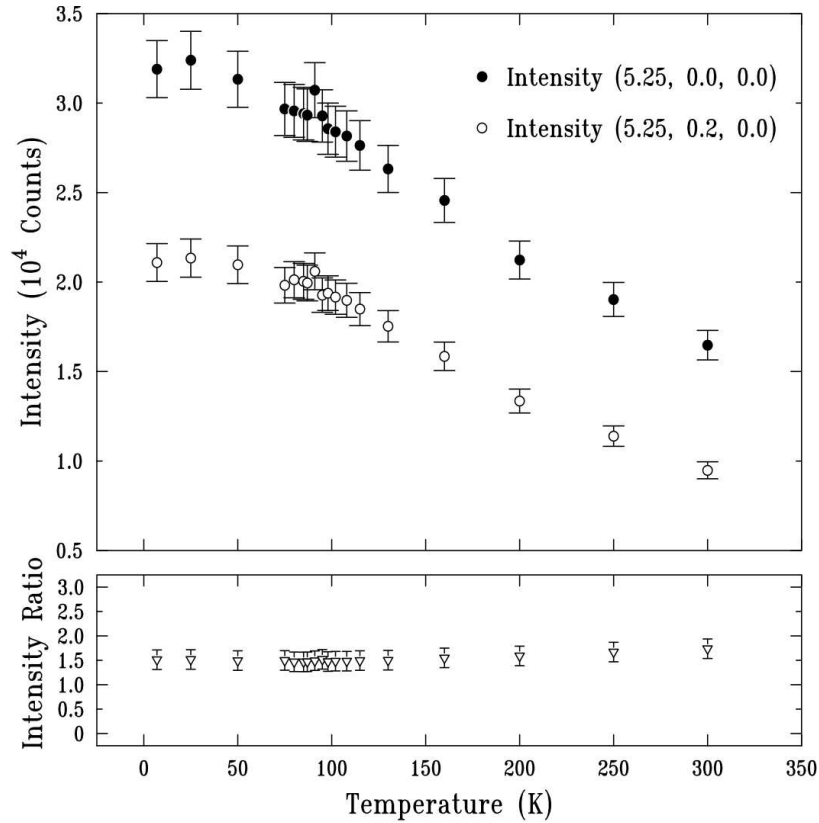


Figure 5.15 Top panel displays the intensity of ORTHO-IV satellite and that of the shoulder structures as a function of temperature. Note that both scale with each other. The ratio of the two intensities as a function of temperature (bottom panel) remains constant within experimental accuracy providing further support that the two modulations are coupled[8].

We need to incorporate the **b**-direction modulation into our ORTHO-IV phase model. As discussed above, the **b**-direction modulation does not form homogeneously throughout the whole crystal. Rather, a $\mathbf{q}_1 = (0, \delta, 0)$ -type wavevector acts as a **b**-direction periodic modulation of the displacements of all the atoms involved in the ORTHO-IV phase. We incorporate this **b**-direction modulation with a simple extension of the ORTHO-IV displacement pattern by replacing $\mathbf{u}'$ s in Eqn. (1) with $\mathbf{t}'$ s as follows:

$$\mathbf{t}_{lk} = \mathbf{u}_{lk}[1 + d \cos(\mathbf{q}_1 \cdot \mathbf{R}_{lk})] \quad (5.15)$$

where l is the index of the unit cells inside the ORTHO-IV phase island and k is the atom index in that unit cell. Since the $\mathbf{u}_{lk}$, as fitted in previous section, lie in the $\mathbf{a}$ - $\mathbf{c}$ plane, the second term of Eqn.(2) represents an additional transverse modulation along the $\mathbf{b}$ -direction. The second term contributes to the $\mathbf{q}_1$ shoulders and has small effects on the center $\mathbf{q}_0$ peaks. Thus the previous fitted values of $\mathbf{u}_{lk}$ are still valid.

With the modified ORTHO-IV phase model, we fit the 2-D diffuse scattering pattern presented in Fig.(5.13a) by considering the scattering from the ORTHO-IV phase islands, the scattering from the associated strain fields and the interference of the scattering from the two, which have been formulated as I_1 , I_2 and I_3 in previous discussion. With the fitted parameters listed in table(5.1), the 2D pattern can be reproduced remarkably well as shown in Fig.(5.16(b)). Fig(5.17) gives a better quantitative view of the data fit along important lines indicated in Fig.(5.16). Thus, our experimental observation and quantitative analyses establish the existence of $\mathbf{b}$ -direction lattice modulation with $\mathbf{q}_1 = (0, \delta \approx 0.21, 0)$ within the ORTHO-IV phase islands in optimally doped YBCO.

Table 5.1 fitting parameters(a and b are lattice constants)

Island Shape function $\langle s(n) \rangle$	w_a	2.8a
	w_b	4.1b
	d_a	1.2a
	d_b	1.6b
pairing correlation function $c(m, n)$	ξ_a	2.65a
	ξ_b	3.18b
$\mathbf{b}$ direction modulation	d	0.9
	δ	$0.21 \frac{2\pi}{b}$
strain field dipole matrix	$\frac{p_{11}}{p_{22}}$	4
	p_{12}, p_{21}	0
	p_{i3}, p_{3j}	not sensitive to

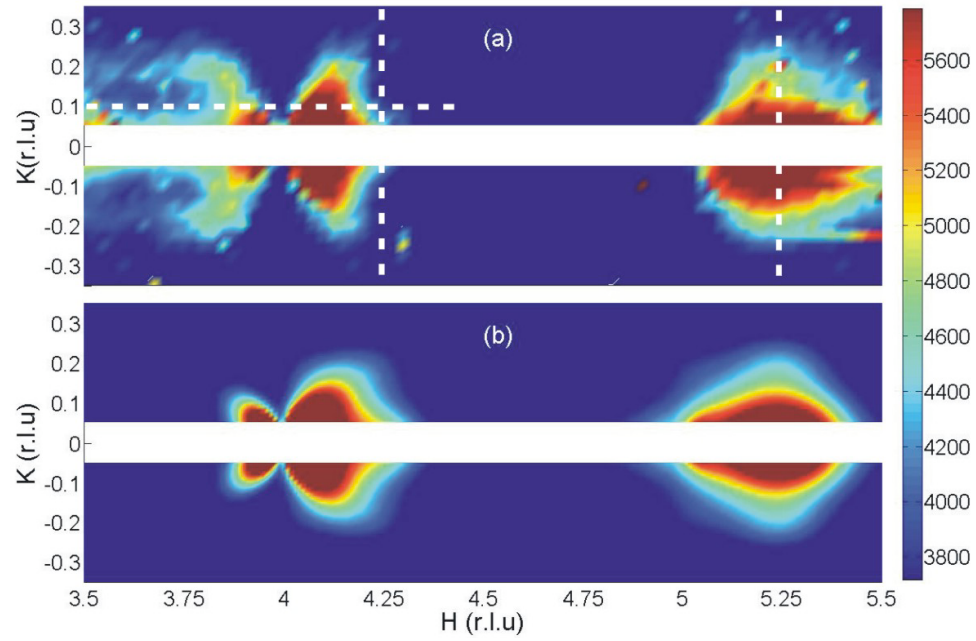


Figure 5.16 (a): Colormap of the measured diffuse scattering around (4, 0, 0) and (5, 0, 0) in H-K plane at $\sim 7K$. (b) Model calculations of the 2D scattering pattern. Asymmetric HDS around (4, 0, 0), q_0 satellite, and q_1 shoulders are all reproduced. The dashed lines indicate the line cuts presented in Fig.(5.17).

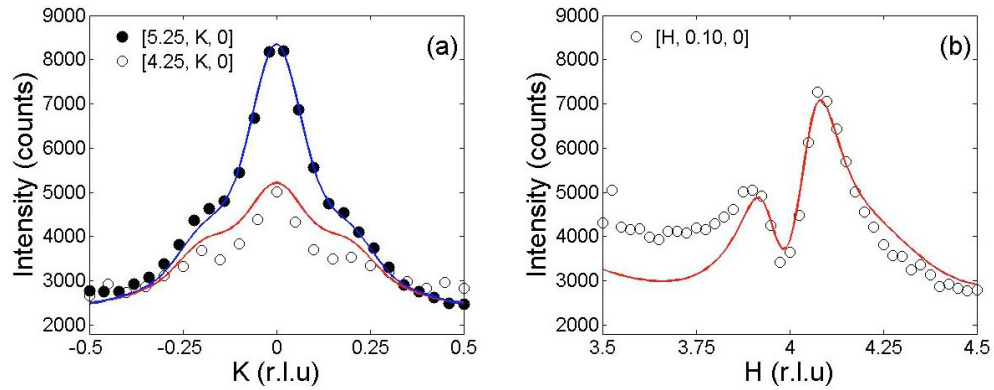


Figure 5.17 Solid lines are the fitting results[8]. δ and d are determined to be 0.21 and 0.9, respectively. The **K** scan in (a) across (4.25, 0, 0) is over estimated by $\sim 13\%$ mainly due to the IFS contribution. The lower side of the **H** scan in (b) is pushed up by the tail of strong (3.25, 0, 0) satellite peak.

5.5.2 Origin of the **b** direction modulation

In fact, searching for the **b** direction modulation in optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been the focus of many experimental works because the theoretically predicted Fermi surface induced instability in this compound.

The optimal doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is distinguished by the presence of CuO chains which are interleaved with CuO_2 bilayers approximately 0.4 nm away. This compound provides the opportunity for the CuO_2 planes to interact with a subsystem of different dimension and symmetry. This uniqueness has attracted a lot of attention, both experimentally[80, 81, 82, 83] and theoretically[84, 85, 86, 87, 88]. The chains are believed to be involved in the superconductivity by having a significant portion of the superfluid density associated with them through proximity effect[80, 83, 89]. They are also involved in the electronic structure of this compound by contributing flat, nested portions of the Fermi surface perpendicular to the $\mathbf{b}^*$ direction with an incommensurate nesting wavevector $\vec{q}_{\text{IC}} = (0, 2k_F \approx 0.22, 0)$ (in reduced lattice units; $\mathbf{k}_F$ is the Fermi wavevector)(Fig.(5.18)), as shown by electronic structure calculations[90], and confirmed by positron annihilation[9] and photoemission[10] studies. Such Fermi surface nesting features are known to give rise to a tendency to an instability against charge density waves(CDW) with the periodicity of $\vec{q}_{\text{IC}}$ and this has led to a number of reports of the existence of such a modulation along the chains.

Evidence for the formation of CDW on the CuO chains has come mainly from surface sensitive scanning tunneling microscopy(STM) measurements[91, 92, 93]. In these measurements, static electronic modulations were observed along the CuO chains with periodicity consistent with the expected $\mathbf{q}_{\text{IC}}$ for an optimally doped YBCO. These modulations

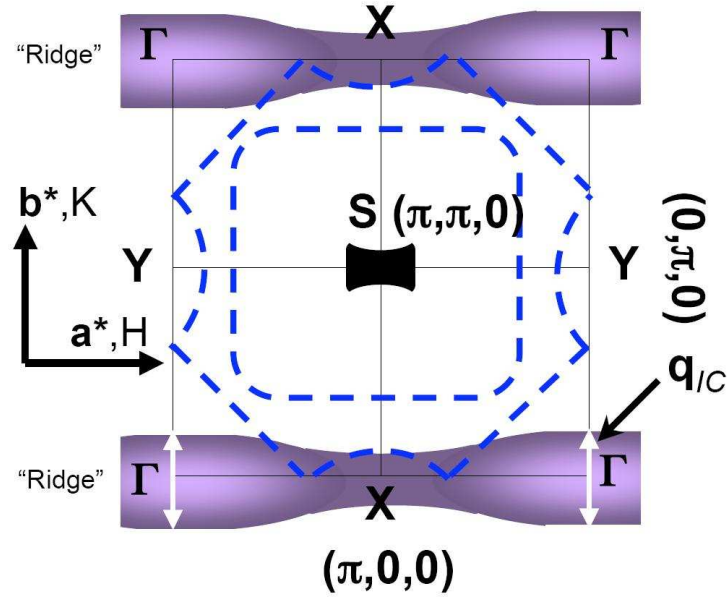


Figure 5.18 A schematic of the Fermi surface for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The ‘ridges’ (purple) are the Fermi surface portions originated from CuO chain planes with nesting vector along $\mathbf{b}^*$ (white)[9, 10].

exhibited short range correlations and their amplitude appeared to be strongest near the clusters of the chain oxygen vacancies. These authors surmised that the observed electronic modulations could result from dynamic CDW pinned by the vacancy clusters. If the STM observed modulations were a general property of the bulk YBCO, the coexistence of the CDW and superconductivity in the chain subsystem would have a significant effect on the superconducting order parameter and complicate our understanding of superconductivity in YBCO. To our knowledge, there has been no conclusive evidence of the formation of CDW on the chains from bulk sensitive measurements so far. Local probes such as NMR/NQR measurements[94, 95, 96] have reported on the formation of CDW on the CuO chains, but the results of different groups are not consistent with each other. Inelastic neutron scattering (INS) measurements[97] have indicated the existence of *dynamical* lattice fluctuations with a wavevector of $(0, \sim 0.23, 0)$, possessing *long-range* coherence. These observations are

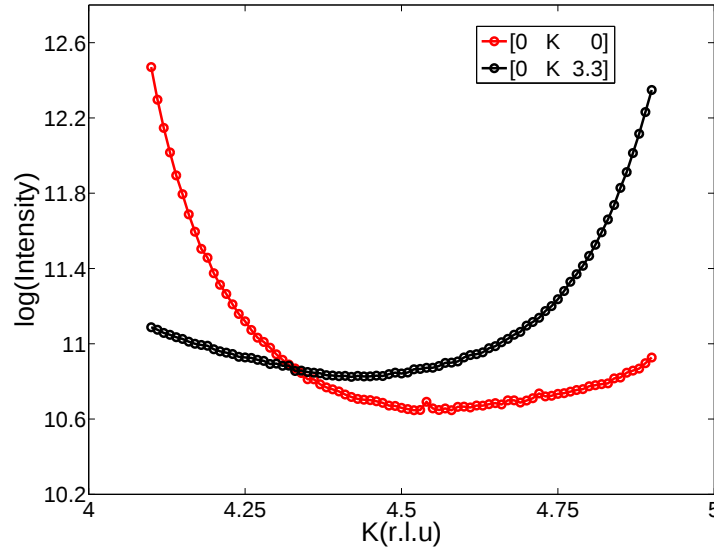


Figure 5.19 K scans in the vicinity of $(m, n, L) \pm \mathbf{q}_{IC}$ at different L values. No superstructure modulation peaks observed in the region of the reciprocal space.

inconsistent with the STM results. Further more, the INS measurements were carried out on a twinned crystal so that order along the $\mathbf{a}^*$ or $\mathbf{b}^*$ axis could not be distinguished.

The *detwinned* sample used in our experiments allows us to unambiguously resolve the $\mathbf{a}$ and $\mathbf{b}$ directions. If lattice modulations associated with CDWs with propagating vector $\vec{q}_{IC}$ are present throughout the whole crystal, they should be observed by X-ray scattering as peaks (or rods) centered at $(m, n, L) \pm \vec{q}_{IC}$ (m and n are integers) in reciprocal space, depending on their inter-chain correlations. A thorough investigation in the vicinity of $(m, n, L) \pm \mathbf{q}_{IC}$ for different integer m and n values showed no indication of such modulations along $\mathbf{b}^*$ direction as claimed by the INS measurements[97]. Two typical scans are shown in Fig.(5.19).

Instead, our quantitative analysis of the X-ray diffuse scattering data revealed the existence of a $\mathbf{b}$ direction lattice modulation which manifests itself as the $\vec{G} \pm \vec{q}_0 \pm \vec{q}_1$

shoulders. The fact that $\vec{q}_1$ is very close to $\vec{q}_{1C}$ strongly indicates that the observed $\mathbf{b}$ -direction modulation within the ORTHO-IV phase islands is induced by the FS effect. In our view, nested ‘ridges’ (or ‘sheets’) of the FS induce a $\vec{q}_1$ amplitude modulation of the ORTHO-IV displacement pattern with a concomitant presence of a CDW on the CuO chains.

The idea that FS nesting can influence short-range order (SRO) and manifest itself in the X-ray diffuse scattering was discussed[98] in the study of order-disorder transitions in binary alloys such as Cu-Au and was used subsequently in investigations[99] of SRO correlated micro-domain structures within a disordered matrix. In the context of the ORTHO-IV phase, any one of the four permutations of $\langle 1110 \rangle$ can form as anti-phase (AP) domains with periodicity along the $\mathbf{b}$ axis determined by $\mathbf{q}_1$. These AP domains would also give shoulders to the $\vec{q}_0$ peaks in scans along the $\mathbf{b}^*$ direction. However, structure-factor calculations based on various combinations (*e.g.* two $\langle 0111 \rangle$ and three $\langle 1110 \rangle$; as illustrated in Fig.(5.18) assuming no amplitude modulations of the ORTHO-IV displacement pattern did not yield relative intensities of $\vec{q}_0$ and $\vec{q}_1$ satellites consistent with the data. Although we can not rule out a more subtle arrangement of AP domains, a simple transverse modulation of a mono-domain ORTHO-IV pattern, as modeled in Eqn.(5.15), adequately accounts for the data.

Our X-ray scattering results are generally consistent with the STM observations[91, 92, 93] which indicate that the CDW’s are pinned by the oxygen vacancies in the CuO chains. Our finding that the $\mathbf{q}_1$ modulations are confined within ORTHO-IV islands seems to differ from STM reports[91, 92, 93] of well-defined electronic corrugations existing in regions *away* from oxygen vacancies. This discrepancy may be due to energetics of CDW

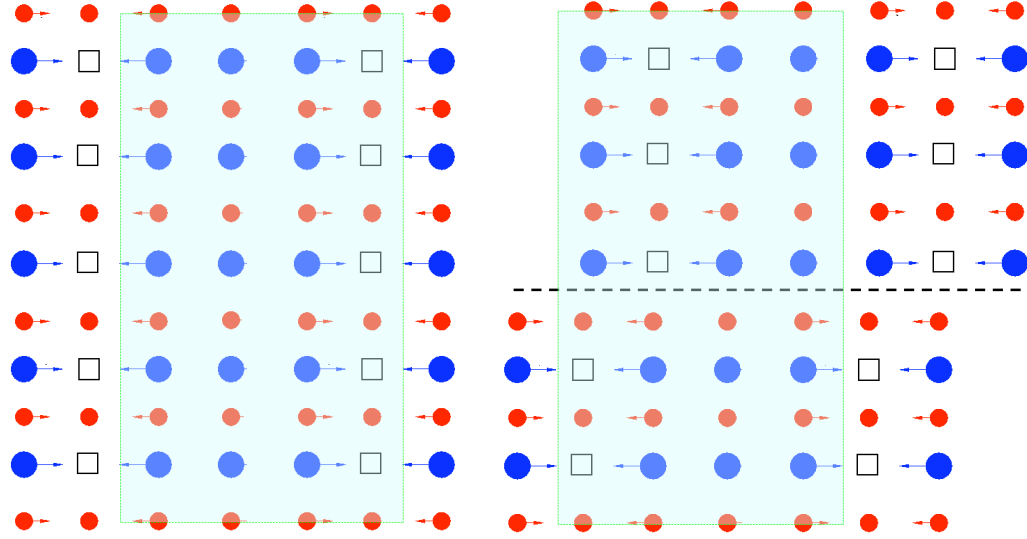


Figure 5.20 Left: ORTHO-IV displacement pattern (ab -plane) for the chains. $\mathbf{q}_1$ further modulates amplitude of these displacements sinusoidally. Right: One possible AP domain with no modulations of displacement amplitudes. Small dots (red): Cu; Big dots (blue): Oxygen; Squares: Vacancy; Dashed line: Domain boundary; Shaded area: 4X5 super-cell. See ref.[8].

formation on chain-terminated surfaces as opposed to that in the bulk. The electronic structure calculations[90] indicate that the CuO chains in the bulk are on the verge of a CDW instability due to FS nesting, but the formation of CDW depends on energy gains of carriers relative to the energy costs of the lattice distortions[100]. The lack of any peaks (or rods) near $(m, n, L) \pm \mathbf{q}_1$ suggests that the formation of CDW is suppressed by the rigidity of the average lattice. Rather, a static CDW can only be well established in favorable regions like a cleaved surface with CuO chains on the first layer where the lattice is inevitably relaxed comparing with the bulk, or in elastically “softer” areas. It has been discussed previously that the abnormal temperature dependent behavior of the intensities of the ORTHO-IV phase satellite peaks indicates the lattice softening in the ORTHO-IV islands, which in principle favors the CDW formation. This agrees well with the STM observations[91, 92, 93] of enhanced CDW amplitudes in the vicinity of oxygen vacancies.

The fact that the $\vec{q}_1$ modulation is confined within the ORTHO-IV phase islands dismisses the concern of coexistence of the CDW and superconductivity on the CuO chain subsystem as a general property of YBCO. Even though $\vec{q}_1$ modulation is driven by the FS nesting of the CuO chains, the shoulders at $\vec{q}_0 \pm \vec{q}_1$ get contributions from the atoms located in the BaO and CuO₂ planes in the ORTHO-IV islands rather than from the chains alone(Eqn.(5.15)). Thus the FS effects perturb the CuO₂ planes within the ORTHO-IV phase islands as well.

5.6 Anisotropy of the strain field

The fitted elements of the strain field dipole matrix are listed in table(5.1). Since the 2-D diffuse scattering data was collected within $\mathbf{a}^*\text{-}\mathbf{b}^*$ plane, all the $\mathbf{c}$ direction related matrix elements are not involved in the fitting.

Even though Eqn.(A.12) used to describe the HDS is empirical, it does reproduce the observed HDS reasonably well. We believe our fitting results does catch the essence of the strain field in YBa₂Cu₃CuO_{6.92}. The fitted ratio of $\frac{p_{11}}{p_{22}} = 4$ indicate that the strain fields associated with the ORTHO-IV phase islands are strongly anisotropic and are much stronger along the $\mathbf{a}$ direction than along the $\mathbf{b}$ direction. This strong anisotropy is expected since the ORTHO-IV phase islands are highly anisotropic. The fitted island widths in table(5.1) show that the islands are elongated along $\mathbf{b}$ direction due to the 1-D nature of the oxygen vacancy ordered empty chains. Thus, the distortion of the host lattice is more likely to be along the $\mathbf{a}$ direction.

The effect of the strong anisotropy of the strain field can be interesting. The in-plane anisotropy of YBCO near optimal doping has been observed in many experiments[101,

102, 103, 104]. The origin of this anisotropy is still an open question. It has been suggested[105, 80] that the one-dimensional CuO chains along the b axis which have weak interactions along the a direction contribute to the superfluid density via proximity effect. The anisotropic strain field we observed here may also play its role. In this case, the anisotropic local strain field acts as a scatterer in the low energy regime with anisotropic scattering strength to the carriers, thus giving rise to the observed in-plane anisotropy. The fact that the strain field is stronger along **a** direction agrees with the observed higher resistivity and lower superfluid density along this direction reported in the above listed literature.

5.7 Summary

In this chapter, the results of our X-ray diffuse scattering experiments on optimally doped $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$ high temperature superconductor were discussed. We found that the majority of the oxygen vacancies tend to cluster together to form 1-D chains in the CuO chain planes. These oxygen vacancy chains are short range ordered to form the ORTHO-IV minority phase islands, which manifest themselves in the X-ray diffuse scattering data as the observed satellite peaks with the relative wavevector $(\frac{1}{4}, 0, 0)$ along **a*** direction. An ORTHO-IV phase model was constructed to fit to the experimental data. Our fitting results show that the typical size of the ORTHO-IV phase islands are of nano-scale(table(5.1)). Within the islands, structural modulation of correlated atomic displacements of Ba, Cu and O atoms, including those in the CuO_2 planes, is induced. Temperature dependent studies show that, as a function of increasing temperature, the intensities of the ORTHO-IV satellite peaks decrease very rapidly, which can not be explained by the temperature

dependence of the Debye-Waller factors. This abnormal temperature dependent behavior indicates that enhanced elastic softening of the lattices takes place within these nano-size islands.

Within these elastically softened ORTHO-IV phase islands, additional **b** direction modulation is revealed by our quantitative analysis. The modulation wavevector, $\vec{q}_1 = (0, 0.21, 0)$, is very close to the nesting vector connecting the flat portions of the Fermi surfaces originated from the CuO chain planes, suggesting the **b** direction modulation is a Fermi surface induced effect. In our view, nested ‘ridges’ (or ‘sheets’) of the FS induce a $\vec{q}_1$ amplitude modulation of the ORTHO-IV displacement pattern with a concomitant presence of a CDW on the CuO chains. The fact that this **b** direction modulation is confined within the elastically softened ORTHO-IV phase islands suggests that the rigidity of the average lattice suppresses the formation of CDW on the CuO chain subsystem as a general property of YBCO.

The ORTHO-IV minority phase islands further induce long range strains to the surround lattice. The strain fields show strong anisotropy along **a** and **b** directions due to the anisotropic nature of the ORTHO-IV islands. We suggest that these strain fields may play their role in the **a-b** anisotropy reported by many transport experiments on YBCO.

Our results clearly show that the YBCO cuprate is intrinsically inhomogeneous. The presence of oxygen vacancy ordered ORTHO-IV minority phase islands and the associated lattice strain sets intrinsic lengths scales ranging from a few unit cells to several nanometers and local anisotropy, both of which can have profound and fundamental influence on electronic properties of $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$. Further, our quantitative analysis shows that the CuO_2 planes are involved in these local lattice distortions. Thus, it is unrealistic to

simplify the superconductivity, at least in optimally doped YBCO, as a single homogeneous phase problem.

This chapter contains materials in

- Z. Islam, X. Liu, S. K. Sinha, J. C. Lang, S. C. Moss, D. Haskel, G. Srajer, P. Wochner, D. R. Lee, D. R. Haefner and U. Welp, “Four-Unit-Cell Superstructure in the Optimally Doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ Superconductor”, *Phys. Rev. Lett.* 93, 157008 (2004). Copyright(2004) by the American Physical Society.
- X. Liu, Z. Islam, S. K. Sinha, S. C. Moss, R. J. McQueeney, J. C. Lang and U. Welp, “Fermi-surface-induced lattice modulation and charge-density wave in optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ”, *Phys. Rev. B* 78, 134526 (2008). Copyright(2008) by the American Physical Society.

A

“Zero”-th order approximation for the diffuse scattering from $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$

In $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$, the details of individual ORTHO-IV phase island can vary from one to the other. For example, they may have different sizes. Also, the empty or full chains within the islands can break up into segments in the sense that the site which is suppose to be empty is actually occupied by an oxygen ion, or vis versa. Due to the breaking of chains and the existence of island boundaries, strictly speaking, there is no well formed superstructure for which $\vec{u}_{lk}$ repeats itself every 4 unit cells along the **a** direction and every one unit cell along the **b** direction. The real situation can be complicated and here we will statistically describe the islands in a phenomenological way with a “zero”-th order model.

The ORTHO-IV islands are constructed in the following way. First, we assume

a perfect YBCO₇ lattice and divide it into blocks which contain 4x1x1 unit cells along **a**, **b** and **c** direction(see Fig.(A.1), respectively. In each block, there are 4 equivalent chain oxygen sites, labeled as V1 V2 V3 and V4. The oxygen vacancies are introduced by taking out oxygen atoms from the *same* site, say V3, from some of the blocks. When those blocks containing oxygen vacancies cluster together, an ORTHO-IV island is formed with the superstructure wavevector to be $(\frac{1}{4}, 0, 0)$. Since the correlation length of the ORTHO-IV phase superstructure modulation along **c** direction is very short(within an unit cell as discussed in previous section), we assume this clustering only happens in the **a-b** plane and the height of the island along **c**-direction is 1 unit cell.

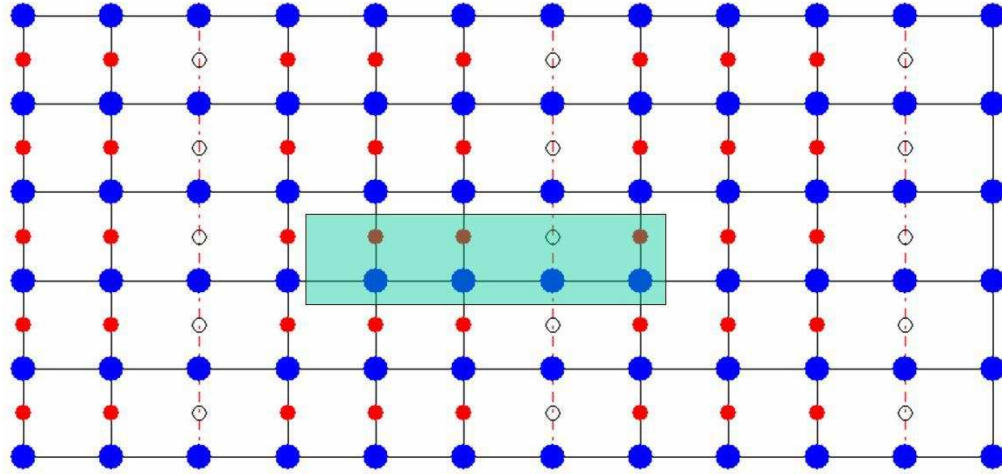


Figure A.1 sketch of the CuO chain plane: perfect clustering of the blocks containing oxygen vacancies to form ORTHO-IV phase. Big dots(blue): Cu; small dots(red): O; circles: oxygen vacancy. The shaded area: 4X1 supercell.

After fixing the island height along **c** direction to be 1 unit cell constant, the construction of the ORTHO-IV phase island is simplified to be a 2-D problem and we will consider the oxygen clustering in the **a-b** plane. The probability of the *m*-th block containing an oxygen vacancy is denoted as $\langle s(m) \rangle$. The real $\langle s(m) \rangle$ might be able to be obtained from

first principle calculations. Here we try to use a reasonable analytical function to simulate the average island shape. In our model, the $\langle s(m) \rangle$ is chosen to be,

$$\langle s(m) \rangle = \frac{z}{2} (\tanh(\frac{w(\hat{R}_m) - |\vec{R}_m|}{d(\hat{R}_m)}) + 1) \quad (\text{A.1})$$

where $\vec{R}_m$ is the center position of m-th block and $\hat{R}_m$ is the direction of the $\vec{R}_m$ vector. $w(\hat{R}_m)$ and $d(\hat{R}_m)$ are direction dependent parameters. With $\langle s(m) \rangle$ defined above, the probability of the m-th block containing an oxygen vacancy is z when it is close to the island center where $|\vec{R}_m|$ is small and the probability is zero when it is far away from the center where $|\vec{R}_m| \gg w(\hat{R}_m)$. So, $w(\hat{R}_m)$ determines the half width of the island along $\vec{R}_m$ direction. $d(\hat{R}_m)$ determines how fast the probability will decrease from z to zero along this direction, meaning the slope of the edge of the average island. Since the oxygen vacancies are very short range ordered, it is conceivable that, even at the center of the islands, there are blocks containing no oxygen vacancies. So, z is not necessarily 1. In our model, it is a free parameter whose value is between 1 and 0.

By choosing $w(\hat{R}_m) = w_a$ and w_b along **a** and **b** directions, we define the general $w(\hat{R}_m)$ to be,

$$w(\hat{R}_m) = \frac{w_a w_b}{\sqrt{(\frac{w_a R_m^b}{R_m})^2 + (\frac{w_b R_m^a}{R_m})^2}} \quad (\text{A.2})$$

where R_m^a and R_m^b are the **a** and **b** direction components of $\vec{R}_m$. With Eqn.(A.2), the average island is defined as having an elliptic shape in the **ab** plane. The slope function, $d(\hat{R}_m)$, is defined in a similar way,

$$d(\hat{R}_m) = \frac{d_a d_b}{\sqrt{(\frac{d_a R_m^b}{R_m})^2 + (\frac{d_b R_m^a}{R_m})^2}} \quad (\text{A.3})$$

where d_a and d_b are the parameters defining the slopes of the edges of the average island along **a** and **b** directions.

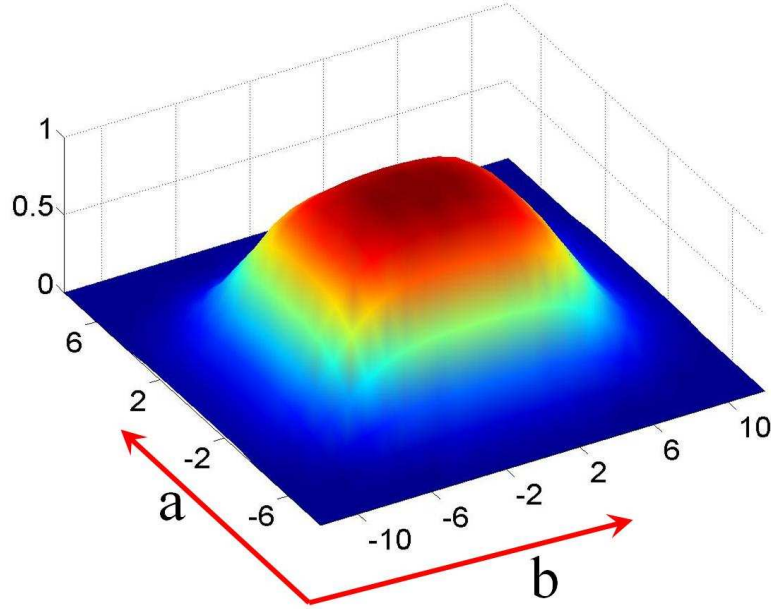


Figure A.2 The average ORTHO-IV phase island shape defined by $\langle s(m) \rangle$ by choosing the parameters to be: $w_a = 5$, $w_b = 8$, $d_a = 1.5$, $d_b = 2.5$ and $z = 1$.

By choosing the parameters to be $w_a = 5$, $w_b = 8$, $d_a = 1.5$, $d_b = 2.5$ and $z = 1$, the shape of the average ORTHO-IV phase island is generated and shown in Fig.(A.2).

Knowing $\langle s(m) \rangle$ is not enough to formulate the X-ray diffuse scattering because the scattering intensity contains the interference between different blocks. We also need to know the joint probability, $\langle s(m)s(n) \rangle$. To carry on our model construction, we need to define the conditional probability $p(s(n) = 1 | s(m) = 1)$, which means: if an oxygen vacancy is found in the m -th block, what is the probability to find an oxygen vacancy in its vicinity blocks, indexed by n . First, this probability depends on where n -th block is. When it is far from the island center, the chance to find oxygen vacancy in it is small and vice versa. Also, it depends on the pairing correlation of the oxygen vacancy distribution. Thus, it has

to be of the form as,

$$p(s(n) = 1 | s(m) = 1) = \langle s(n) \rangle c(m, n) \quad (\text{A.4})$$

In our toy model, the pairing correlation function of the oxygen vacancy distribution, $c(m, n)$ is defined as,

$$c(m, n) = e^{-\sqrt{(\frac{\vec{R}_{mn}^a}{\xi_a})^2 + (\frac{\vec{R}_{mn}^b}{\xi_b})^2}} \quad (\text{A.5})$$

where $\vec{R}_{mn}$ is the displacement vector between the m -th and n -th blocks. The parameters, ξ_a and ξ_b , define the pairing correlation lengths of the oxygen vacancies along **a** and **b** directions. If the ORTHO-IV phase island is “perfectly” formed with the blocks containing oxygen vacancies to be tightly packed, we have $z = 1$. For this scenario, ξ_a and ξ_b are infinitely long and $c(m, n)$ is essentially 1.

With the conditional probability defined above, we have,

$$\langle s(m)s(n) \rangle = \langle s(m) \rangle \langle s(n) \rangle c(m, n) \quad (\text{A.6})$$

In the following, the three different contributions to the overall diffuse scattering intensity defined in Eqn.(5.9) Eqn.(5.10) and Eqn.(5.11) will be discussed respectively based on the “toy model” constructed above.

In principle, the lattice distortion pattern in the m -th blocks containing an oxygen vacancy, $\vec{u}_{hk}^m$ (h is the unit cell index within a block and k is the index of atoms within an unit cell), also depends on its neighbors. The more closely the ORTHO-IV islands are packed ($z \rightarrow 1$), the more uniform the $\vec{u}_{hk}^m$ will be. “uniform” is in the sense that $\vec{u}_{hk}^m$ repeat themselves from one block to the other. The absence of an oxygen vacancy in the nearest and second nearest supercells can be treated as first order and second order perturbations

to $\vec{u}_{hk}^m$. Also, the presence of the oxygen vacancy within the m -th block will perturb the surrounding blocks no matter whether there are oxygen vacancies in them or not. In this Toy model, we take only “zero”-th order approximation by assuming that $\vec{u}_{hk}^m$ is the same for all blocks containing oxygen vacancy and are zero for those blocks without oxygen vacancies. The non-zero distortion vectors $\vec{u}_{hk}$ for the blocks containing oxygen vacancies will be denoted as $\vec{u}_{hk}^0$ in the following discussion. Thus the statistical problem of $\vec{u}_{hk}^m$ to be $\vec{u}_{hk}^0$ or zero is equivalent to the problem of finding the m -th block to have oxygen vacancy or not. With this approximation, the scattering purely from the ORTHO-IV phase island, I_1 , can be written as,

$$\begin{aligned}
I_1 &= N_0 < \left| \sum_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} (e^{i\vec{Q} \cdot \vec{u}_{lk}} - 1) \right|^2 > \\
&= N_0 < \sum_{\substack{m h k \\ m' h' k'}} \tilde{f}_{hk}^m \tilde{f}_{h'k'}^{*m'} e^{i\vec{Q} \cdot \vec{R}_{hk}^m} e^{-i\vec{Q} \cdot \vec{R}_{h'k'}^{m'}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^m} - 1) (e^{-i\vec{Q} \cdot \vec{u}_{h'k'}^{m'}} - 1) > \\
&= N_0 \sum_{\substack{h k \\ h' k'}} \tilde{f}_{hk} \tilde{f}_{h'k'}^* e^{i\vec{Q} \cdot (\vec{R}_{hk} - \vec{R}_{h'k'})} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) (e^{-i\vec{Q} \cdot \vec{u}_{h'k'}^0} - 1) \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} < s(m) s(m') > \\
&= N_0 \left| \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \right|^2 \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} < s(m) s(m') > \\
&= N_0 \left| \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \right|^2 \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} < s(m) > < s(m') > c(m, m')
\end{aligned} \tag{A.7}$$

The first summation in Eqn.(A.7) is the structure factor of the ORTHO-IV phase supercell and the second summation is essentially an envelope function which gives peaks at $(\frac{n}{4}, 0, 0)$ positions in reciprocal space as observed.

Next, we will consider the scattering from the strain field, I_2 . According to

Eqn.(5.10), I_2 can be written as,

$$I_2 = N_0 < \left| \sum_{lk} i\vec{Q} \cdot \vec{v}_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} + \sum_{lk} i\vec{Q} \cdot \vec{v}_{lk} \tilde{f}_{lk} e^{i\vec{Q} \cdot \vec{R}_{lk}} (e^{i\vec{Q} \cdot \vec{u}_{lk}} - 1) \right|^2 > \quad (\text{A.8})$$

From the fitting results which will be discussed later, we know that, for some of the atoms, $\vec{u}_{hk}^0$ are large and it is not proper to only expand $e^{i\vec{Q} \cdot \vec{u}_{hk}^0}$ to first order. Thus, we can not assume that $(e^{i\vec{Q} \cdot \vec{u}_{lk}} - 1)$ is much smaller than 1 and directly ignore the second term. But this is true for only a very small portion of the atoms inside the ORTHO-IV phase island which have relatively large $\vec{u}_{hk}^0$. Also, the summation of the second term is confined within a much smaller region comparing with the first summation because $\vec{u}_{lk}$ is non-zero only inside the ORTHO-IV phase islands. Because of these two reasons, the second term ends up to be much smaller than the first term. In the following discussion, the second summation will be neglected and only the leading term(the first summation) will be considered.

The strain field associated with defect clusters is complicated. It not only depends on the defect distribution within the clusters, but also depends on the elastic property of the clusters comparing with the average lattice. A simple treatment has been carried out by P.H.Dederichs[34, 79] and other authors[35, 106], assuming the lattice distortion of the strain field is small and the elastic property of the clusters is the same as the average lattice. Then the strain fields associated with different defects will be independent of each other and the lattice distortions introduced by individual defects can be linearly added up. These assumptions have been made in section **3.3.5** in the discussion of HDS from multiple defect centers. Here we extend the discussion to the diffuse scattering from $\text{YBa}_2\text{Cu}_3\text{CuO}_{6.92}$, assuming the assumptions are applicable here.

With the above assumptions, the total $\vec{v}_{lk}$ can be written as,

$$\vec{v}_{lk} = \sum_m s(m) \vec{v}_{lk}^m \quad (\text{A.9})$$

where $\vec{v}_{lk}^m$ are the lattice distortion vectors introduced by single oxygen vacancy in the m -th block. $s(m)$ gives the oxygen vacancy occupation for a certain island, whose statistical average over all islands is $\langle s(m) \rangle$. Since we assume individual defects induce the same lattice distortion, we have,

$$\vec{v}_{l_1 k}^{m_1} = \vec{v}_{l_2 k}^{m_2} \quad (\text{A.10})$$

if the relative position of the l_1 -th unit cell to the center of m_1 -th block is the same as l_2 -th unit cell to the center of m_2 -th block. $\vec{v}_{lk}^m$ does not depend on the m index and we re-denote it as $\vec{v}_{jk}^0$ where j is relative to the center of a block containing oxygen vacancy. Thus, analogously to Eqn.(3.40) and Eqn.(3.41), we have,

$$\begin{aligned} I_2 &= N_0 \left\langle \left| \sum_m s(m) e^{i\vec{Q}\vec{R}_m} \sum_{lk} \vec{Q} \vec{v}_{lk}^m \tilde{f}_{lk} e^{i\vec{Q}(\vec{R}_{lk} - \vec{R}_m)} \right|^2 \right\rangle \\ &= N_0 \left\langle \left| \sum_m s(m) e^{i\vec{Q}\vec{R}_m} \sum_{jk} \vec{Q} \vec{v}_{jk}^0 \tilde{f}_{jk} e^{i\vec{Q}\vec{R}_{jk}} \right|^2 \right\rangle \\ &= N_0 \left| \sum_{jk} \vec{Q} \vec{v}_{jk}^0 \tilde{f}_{jk} e^{i\vec{Q}\vec{R}_{jk}} \right|^2 \sum_{mm'} e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_{m'})} \langle s(m) \rangle \langle s(m') \rangle c(m, m') \end{aligned} \quad (\text{A.11})$$

The above equation is similar to Eqn.(A.7) which describes the ORTHO-IV phase satellite peaks. In Eqn.(A.11), the first summation essentially describes the HDS due to single oxygen vacancy and the second summation gives an envelope function which peaks at $(\frac{n}{4}, 0, 0)$

positions in reciprocal space.

Interestingly, the observed $(\frac{n}{4}, 0, 0)$ satellite peaks clearly shows the modulation effect of the second summation in Eqn.(A.7), but we do not see the modulation effect on the HDS as described in Eqn.(A.11), as shown in Fig.(5.6). Computer simulation based on Eqn.(A.11) gives a totally different HDS pattern comparing with the experimentally observed data. Thus, the simple linear-adding-up approximation is not applicable to the strain field associated with the ORTHO-IV phase islands. This is consistent with the abnormal temperature dependent behavior of the ORTHO-IV satellite peaks discussed in previous section. There we came to the conclusion that elastic softening happens within the ORTHO-IV phase islands. Thus, the elastic properties are different for the ORTHO-IV phase islands comparing with the average lattice and the lattice distortions induced by oxygen vacancies at the center of the islands are expected to be different from that induced by oxygen vacancies at the edge.

Since detailed information of the elastic properties of the ORTHO-IV phase islands is not available, we can not give a rigorous derivation of I_2 for this very complicated case. Further more, the propagation of lattice distortion within the islands may not be described with macroscopic elastic theory at all because the local lattice distortions are inhomogeneous due to the very short range order of the oxygen vacancies. On the other hand, we noticed that the observed HDS can be described reasonably well by Eqn.(3.37) without considering the detailed island configuration. Thus, as a “zero”-th order model, we treat the ORTHO-IV island as a whole “big” defect and write I_2 as,

$$I_2 = N_0 < |\frac{-1}{M} \sum_{k\alpha} \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} Q_\alpha \sum_{\beta} \mathbb{D}_{\alpha\beta}^{-1} \sum_{\gamma} p_{\beta\gamma} q_{\gamma}|^2 > \quad (\text{A.12})$$

following Eqn.(3.39). Note that this is *empirical* and we use Eqn.(A.12) to describe the lattice strain *outside* of the ORTHO-IV phase islands, from which the scattering dominates the observed HDS. Small p is used here to distinguish it from the P matrix used in Chapter 3 Eqn.(3.39) to formulate the HDS from single defect since p matrix here does not necessarily have the same microscopic meaning as the P matrix defined previously.

To carry out the averaging in Eqn.(A.12), we need to know not only the average of the p matrices for the strain fields associated with different ORTHO-IV phase island realizations, but also the standard deviation of the p matrices, which is again unknown. In the following discussion, we assume the standard deviation of the p matrices is much smaller than the average $\bar{p}$. Thus, we substitute the p matrix in Eqn.(A.12) with $\bar{p}$ to keep only the “zero”-th order term from the average and I_2 becomes,

$$I_2 = N_0 \left| \frac{1}{M} \sum_k \tilde{f}_k e^{i\vec{G} \cdot \vec{R}_k} \sum_{\alpha\beta\gamma} Q_\alpha \mathbb{D}_{\alpha\beta}^{-1} \bar{p}_{\beta\gamma} q_\gamma \right|^2 \quad (\text{A.13})$$

Following the above arguments, the diffuse intensity due to the interference between the scattering from the ORTHO-IV phase island and associated strain field, I_3 , can be written as,

$$I_3 = -\frac{N_0}{M} \sum_{hk} \tilde{f}_{hk} e^{i\vec{Q} \cdot \vec{R}_{hk}} (e^{i\vec{Q} \cdot \vec{u}_{hk}^0} - 1) \sum_m e^{i\vec{Q} \cdot \vec{R}_m} \langle s(m) \rangle \sum_{k'} \tilde{f}_{k'} e^{i\vec{G} \cdot \vec{R}_{k'}} \sum_{\alpha\beta\gamma} Q_\alpha \mathbb{D}_{\alpha\beta}^{-1} \bar{p}_{\beta\gamma} q_\gamma + c.c. \quad (\text{A.14})$$

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