NEUTRON SCATTERING STUDIES
OF THE
MAGNETISM AND LATTICE DYNAMICS IN La_{2-x}Sr_xCuO_4

by

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ABSTRACT

Neutron scattering experiments on the La_{2-x}Sr_xCuO_4 class of high-T_c superconductors have been done at the High Flux Beam Reactor at Brookhaven National Laboratory. Two aspects of the La_{2-x}Sr_xCuO_4 system, the lattice dynamics and the magnetism, were examined. In the lattice dynamics studies, the soft phonon modes associated with a structural phase transition in the material have been investigated. This work elucidated the nature of various low temperature structural anomalies, and established that these structural anomalies are not related to the superconductivity in an important way. In the magnetism studies, four important discoveries were made: (1) Two dimensional antiferromagnetic correlations which can be described by the S = \frac{1}{2} Heisenberg model exist in La_2CuO_4, and the theory of this model deduced by Chakravarty, Halperin, and Nelson quantitatively accounts for the experimental results. (2) Magnetic fluctuations which have a correlation length comparable to the superconducting coherence length exist in superconducting La_{2-x}Sr_xCuO_4. (3) The magnetic correlations in nonsuperconducting samples are antiferromagnetic in nature, while superconducting samples have magnetic correlations indicative of an incommensurate spin state. (4) Superconducting samples exhibit a gap in their spin excitation spectrum comparable to the superconducting quasiparticle gap, while nonsuperconducting samples have no such gap.

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Title: Cecil and Ida Green Professor of Physics and Department Head
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To Kazu Yamada I owe much for his patience and perseverance during many challenging experiments at Brookhaven. I am also grateful to Kazu and his family for their warm hospitality.

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Finally, I would like to thank my family for their love and support.
I know where the road to nowhere is, it's highway 89...
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1. Introduction

In 1986, J. G. Bednorz and K. A. Müller published an article\(^1\) on the possible existence of "high-\(T_c\) superconductivity in the Ba-La-Cu-O system." This paper initiated intense research activity, largely because of the potential applications of high temperature superconductors, but also because of the interesting scientific issues raised by this phenomenon. Superconductivity at temperatures up to 125K has since been discovered in a number of oxides;\(^2-6\) table 1.1 lists representative materials from all known classes of the high-\(T_c\) superconductors, along with their superconducting transition temperatures.

\[
\begin{array}{l|c}
\text{Material} & \text{\(T_c\) (K)} \\
\hline
\text{La}_{2-x}\text{Sr}_x\text{CuO}_4-\gamma & 38 \\
\text{YBa}_2\text{Cu}_3\text{O}_7 & 93 \\
\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8 & 85 \\
\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} & 125 \\
\text{Ba}_x\text{K}_{1-x}\text{BiO}_3 & 30 \\
\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 & 24 \\
\end{array}
\]

The fact that \(T_c\) in these materials is so large is unusual enough in itself; it is even more surprising that the high-\(T_c\) superconductivity occurs in oxides, since oxides are more often than not insulators. Indeed, many properties of the high-\(T_c\)

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superconductors are quite different from conventional superconductors. Consequently it is now widely believed that a different microscopic mechanism is causing the superconductivity in the high-$T_c$ superconductors.

This thesis will discuss neutron scattering experiments performed on one of the classes of high-$T_c$ superconductors, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system. Two general subjects have been examined, the lattice dynamics and the magnetism. No evidence linking the lattice dynamics to the superconductivity was found, but interesting behavior related to a structural transition in the material has been investigated. On the other hand, very strong evidence associating the superconductivity with magnetic behavior has been observed, and the experimental results described herein have stimulated much theoretical work on magnetic models of the superconductivity.

The organization of the thesis is as follows. In chapter 2 an overview of the physical properties of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system will be presented. Some of the theoretical approaches that have been used to analyze the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system are discussed in chapter 3. A review of the neutron scattering experimental technique, along with other experimental details, is presented in chapter 4. In chapter 5 experiments on the lattice dynamics associated with a structural phase transition, along with the Landau theory of this transition, are presented. Neutron scattering experiments on the magnetic behavior of insulating $\text{La}_2\text{CuO}_4$ and their relationship to current theories of the 2-D $S=\frac{1}{2}$ Heisenberg model are discussed in chapter 6, and in chapter 7 experiments on the magnetic behavior of metallic and superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ are presented. Finally, in chapter 8 the relationship of the experimental results to current theories of the superconductivity is examined.
2. Physical Properties of La$_{2-x}$Sr$_x$CuO$_{4-y}$

In this chapter the experimental work which has elucidated some of the basic properties of the La$_{2-x}$Sr$_x$CuO$_{4-y}$ system will be discussed. In section 2.1 the structural properties are introduced, including a brief description of the lattice dynamics and structural phase transitions present. Transport properties are examined in section 2.2, and the rudiments of the magnetic phenomena present are discussed in 2.3. Some of the unusual properties of the superconducting state are reviewed in 2.4. In section 2.5, the results of spectroscopic experiments are presented. This chapter is not a comprehensive review of the physical properties of La$_{2-x}$Sr$_x$CuO$_4$; only those aspects which are essential for understanding the remainder of this thesis will be discussed. Additional reviews may be found in the articles by Bednorz and Muller,$^1$ Tinkham and Lobb,$^2$ and a book edited by Ginsberg.$^3$

Many of the physical properties of the La$_{2-x}$Sr$_x$CuO$_4$ system are summarized in the phase diagram$^4$ shown in figure 2.1. In addition to the superconducting transition, a variety of other transitions can occur in this material. These include a transition between phases which have tetragonal and orthorhombic structures, magnetic transitions into either 3-D Néel or spin glass states, and transitions in the conductivity from insulating to metallic states.

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Figure 2.1. Phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The unusual richness of the behavior exhibited in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ makes the study of the system both challenging and interesting. In order to understand even one aspect of this system, a reasonable knowledge of all aspects of the system is necessary because the transitions in the magnetic, structural and transport properties are all interrelated. For this reason, a variety of different aspects of the system will be described, even though this thesis will only examine structural and magnetic phenomena.
2.1 Structural Properties

The crystal structure of $\text{La}_2\text{CuO}_4$ is shown in figure 2.2.

![Crystal Structure of $\text{La}_2\text{CuO}_4$](image)

**Figure 2.2.** Crystal Structure of $\text{La}_2\text{CuO}_4$

At high temperatures the structure is body-centered tetragonal, space group $I4/mmm$, with one $\text{La}_2\text{CuO}_4$ formula unit per primitive cell. At a temperature $T_0$, which is ~530K in stoichiometric material, the crystal undergoes a second order transition to the orthorhombic phase, space group Cmca, which has two formula units per unit cell.\(^1\)

The open arrows in figure 2.2 show the displacements of oxygen ions in the low temperature phase. The transition involves primarily a staggered rotation of the $\text{CuO}_6$ octahedra about either a $(110)_T$ or $(\overline{1}10)_T$ axis; here the subscript $T$ implies that one is using a tetragonal cell. For the remainder of this thesis, if the indices are not indexed by a $T$, then orthorhombic units will be understood. The temperature of this structural phase transition at different strontium concentrations\(^2\) can be found in figure 2.1. $T_0$

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also depends on the oxygen concentration;\textsuperscript{1} figure 2.1 does not show this aspect of the behavior, however.

Atomic positions for both the tetragonal and orthorhombic structures are given in table 2.1. Typical values for the lattice constants of La\textsubscript{2}CuO\textsubscript{4} are \(a = b = 3.82\text{"A}\) and \(c = 13.2\text{"A}\) in the tetragonal phase, and \(a = 5.36\text{"A}\), \(b = 13.15\text{"A}\) and \(c = 5.41\text{"A}\) in the orthorhombic phase. A peculiarity of the Cmca space group notation is that the tetragonal \(c\) axis becomes the orthorhombic \(b\) axis; most researchers use the Cmca notation, however, so one must adjust to it.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\multicolumn{2}{|c|}{tetragonal phase} & \multicolumn{2}{|c|}{orthorhombic phase} \\
atom & position & atom & position & atom & position \\
\hline
La(1) & (0,0,0.37) & La(1) & (-0.02,0.35,0) & La(2) & (0.48,0.15,0) \\
La(2) & (0,0,-0.37) & La(3) & (0.02,-0.35,0) & La(4) & (-0.48,-0.15,0) \\
Cu & (0,0,0) & Cu(1) & (0,0,0) & Cu(2) & (0.50,0.50,0) \\
O(1) & (0,0,0.19) & O(1) & (-0.15,0.18,0) & O(2) & (0.35,0.32,0) \\
O(2) & (0,0,-0.19) & O(3) & (0.15,0,-0.18) & O(4) & (-0.35,-0.32,0) \\
O(3) & (0,-0.50,0) & O(5) & (0.25,0.06,0.25) & O(6) & (-0.25,-0.06,0.25) \\
O(4) & (0.50,0,0) & O(7) & (0.25,0.06,-0.25) & O(8) & (-0.25,-0.06,-0.25) \\
\hline
\end{tabular}
\end{table}

When La\textsubscript{2}CuO\textsubscript{4} is doped with strontium, neutron scattering experiments have shown that the strontium occupies sites formerly occupied by lanthanum ions.\textsuperscript{2} Oxygen defects are also present; the positions of extra oxygen ions and oxygen vacancies are not currently known, however.

\begin{itemize}
\end{itemize}
Since superconductivity in conventional systems arises from electron-phonon interactions, a structural aspect of the La$_{2-x}$Sr$_x$CuO$_{4-y}$ system which is clearly of interest is the behavior of the phonon modes. In figure 2.3 the dispersion of some of the low energy phonon modes measured in neutron scattering experiments done by Böni et al. is shown.$^1$

![Diagram showing dispersion of low energy phonon modes in La$_2$CuO$_4$](image)

**Figure 2.3. Dispersion of Low Energy Phonon Modes in La$_2$CuO$_4$**

An important phonon branch in this figure is the transverse optic $\Sigma_4$ mode, the temperature dependence of which is shown in the inset. This soft phonon is

---

responsible for the tetragonal to orthorhombic structural transition,\textsuperscript{1} as discussed in chapter 5. The dispersion curves of the rest of the low lying phonon modes are only weakly temperature dependent, and are not abnormal in any way. The high energy phonon modes have been studied in Raman\textsuperscript{2} and infrared\textsuperscript{3} experiments, from which it has been found that the largest phonon energies are \( \sim 120 \text{meV} \). These studies also did not report any convincing evidence which indicated that phonons are responsible for the superconductivity.

In the conventional phonon mediated superconductors, the materials with the highest transition temperatures often are structurally unstable. It is natural therefore that much work has been devoted to searching for structural instabilities in the high\( -T_c \) superconductors. In figure 2.4 a measurement of the sound velocity versus temperature in \( \text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4 \) done by Fossheim \textit{et al.} is shown.\textsuperscript{4} The tetragonal to orthorhombic transition occurs at \( \sim 190 \text{K} \) in this sample, and the superconducting transition occurs near 30K. At high temperatures the acoustic modes are quite stiff, suggesting that the system is structurally stable, while at \( T_0 \) the velocity decreases dramatically. Not surprisingly, this behavior is related to the structural transition.

Figure 2.4. Sound Velocity of La$_{1.85}$Ba$_{0.15}$CuO$_4$

The most interesting aspect of the sound velocity is that it remains soft for an extended temperature range below $T_0$, which implies that the Cmca phase is structurally unstable. Further, a hardening of the acoustic modes near 60K can be seen. This behavior is highly suggestive; a thorough investigation to see whether it is related to the superconductivity is described in chapter 5 of this thesis.
2.2 Transport Properties

The transport properties of La$_{2-x}$Sr$_x$CuO$_{4-y}$ are fascinating because of the unusual variation that occurs in them when the hole concentration is changed by only a few percent. In undoped La$_2$CuO$_4$, the resistivity is as high as $10^8$ $\Omega$cm at 5K, while in samples with strontium concentrations of just 0.07 the sample is superconducting at this same temperature. This insulator-metal transition is one of the most important aspects of the La$_{2-x}$Sr$_x$CuO$_{4-y}$ system; indeed, proximity to an insulator-metal transition appears to be a prerequisite for high-$T_c$ superconductivity.

The charge of the carriers can be found from simple ionic valence state arguments. Lanthanum prefers to be in a +3 state, while strontium prefers to be +2; so when strontium replaces lanthanum, electrons are acquired by the strontium ions and hole carriers created. This argument has been confirmed by Hall effect and thermopower measurements.$^1$ The oxygen content can also be changed in the La$_{2-x}$Sr$_x$CuO$_{4-y}$ system by annealing. When excess oxygen is introduced, it probably forms O$_2^-$ superoxide ions,$^2$ and the hole concentration is increased. When oxygen is removed, it changes from a $-2$ state in the crystal to a neutral state as O$_2$ gas, and electrons are donated to the crystal in the process. The net hole concentration of a sample, $p$, appears to control most of the magnetic and transport properties.

In figure 2.5 the resistivity versus temperature of samples with strontium

concentrations, x, of 0, 0.06 and 0.15 is shown.\footnote{Kastner, M. A., \emph{et al.}, Phys. Rev. B 37, 111 (1988); Shirane, G., \emph{et al.}, Phys. Rev. Lett. 63, 330 (1989); Thurston, T. R., \emph{et al.}, Phys. Rev. B 40, (1989).} A common feature of the resistivity at all concentrations is the anisotropy present in the normal state; the resistivity along the b axis is typically 10–300 times larger than within the a–c plane. This anisotropy suggests that for many purposes La$_{2-x}$Sr$_x$CuO$_{4-y}$ may be regarded as weakly coupled CuO$_2$ sheets which become metallic with doping. In the following discussion only the in-plane 2-D resistivity of the copper oxide sheets will be considered.
Figure 2.5. Resistivity of $x = 0$, 0.06 and 0.15 samples of La$_{2-x}$Sr$_x$CuO$_{4-y}$
In the undoped sample, the resistivity can be adequately fit with the Mott hopping law, \( \rho = \rho_0 \exp(T_0/T)^{m} \). As discussed in chapter 3, this form for the resistivity is expected when the carriers hop between disorder induced localized electronic states; the carriers reside in a nonperiodic array of potential energy wells, and they tend to get trapped in the deeper wells rather than propagate through the system. Detailed studies\(^2\) of the Hall coefficient and dielectric constant in oxygen doped samples indicate that the localization length of the carriers within the CuO\(_2\) sheets approaches ~10 Å as the carrier concentration approaches zero.

The resistivity of the x = 0.06 sample increases with decreasing temperature over the entire range measured, 300K to 5K. This may lead one to conclude that the sample is insulating; however, measurements of the dielectric constant\(^2\) indicate that a 2-D insulator-metal transition occurs at \( p \approx 0.01 \). A plausible explanation for this apparent contradiction lies in the two dimensional nature of the system. It turns out that in 2-D metals the resistivity actually increases with decreasing temperature because of constructive interference effects which enhance carrier backscattering processes.\(^3\) The effect is known as weak localization, and it will occur whenever even a small amount of disorder is present in the sample. Experimental work\(^4\) to test this hypothesis is currently being done.

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4. Preyer, N. W., et al., ongoing work.
In the undoped sample, the resistivity can be adequately fit with the Mott hopping law, \( \rho = \rho_0 \exp(T_0/T)^\nu \). As discussed in chapter 3, this form for the resistivity is expected when the carriers hop between disorder induced localized electronic states; the carriers reside in a nonperiodic array of potential energy wells, and they tend to get trapped in the deeper wells rather than propagate through the system. Detailed studies\(^2\) of the Hall coefficient and dielectric constant in oxygen doped samples indicate that the localization length of the carriers within the CuO\(_2\) sheets approaches \(-10\) Å as the carrier concentration approaches zero.

The resistivity of the \( x = 0.06 \) sample increases with decreasing temperature over the entire range measured, 300K to 5K. This may lead one to conclude that the sample is insulating; however, measurements of the dielectric constant\(^2\) indicate that a 2-D insulator-metal transition occurs at \( p \approx 0.01 \). A plausible explanation for this apparent contradiction lies in the two dimensional nature of the system. It turns out that in 2-D metals the resistivity actually increases with decreasing temperature because of constructive interference effects which enhance carrier backscattering processes.\(^3\) The effect is known as weak localization, and it will occur whenever even a small amount of disorder is present in the sample. Experimental work\(^4\) to test this hypothesis is currently being done.

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4. Preyer, N. W., et al., ongoing work.
The sample with the superconducting transition, the p=0.15 sample, also exhibits apparent weak localization behavior, since the resistivity increases just above the superconducting transition. An alternative explanation of this increase in the resistivity is given in reference 1; this work also discusses the linear temperature dependence of the normal state resistivity. Typically, the resistivity of a metal arises from either electron-phonon or electron-electron scattering processes, which usually have $T^2$, $T^3$ or $T^4$ temperature dependences for temperatures less than 300K. The linear temperature dependence of the normal state resistivity is therefore quite unusual; one possibility is that it arises from strong coupling of the carriers to magnetic excitations.\(^1\)

Another intriguing aspect of the resistivity in this system is that samples with strontium concentrations greater than ~0.30 do not undergo a superconducting transition (see figure 2.1).\(^3\) The samples are nonetheless metallic. Within the context of magnetic models of the superconductivity, this behavior may be related to the destruction of the moments, or changes in the magnetic state of the system.

\(^{1}\) Anderson, P. W., Zou, Z., Phys. Rev. Lett. 60, 132 (1988);
2.3 Magnetic Properties

If one assumes that the bonding is primarily ionic in La$_2$CuO$_4$, then the valence state of the copper ions is +2, and their electronic configuration is 3d$^9$. This suggests that La$_2$CuO$_4$ will exhibit magnetic behavior. Further, since crystal field effects usually quench orbital moments in transition metal compounds, the magnetic moment in La$_2$CuO$_4$ would have a spin only moment of $S = \frac{1}{2}$.

Neutron scattering experiments done by Vaknin et al.\textsuperscript{1} first demonstrated that long range magnetic order exists in La$_2$CuO$_4$. A transition to a three dimensional Néel state was found to occur; the spin structure of this antiferromagnetic state is shown with the black arrows in figure 2.6.

![Diagram of La$_2$CuO$_4$ spin structure](image)

Figure 2.6. Spin Structure of La$_2$CuO$_4$

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In addition, the spins have a small cant in the orthorhombic b direction; this canting is the origin of the hidden weak ferromagnetism discovered by Thio et al.\textsuperscript{1} The antiferromagnetic exchange constant for interactions within the CuO$_2$ sheets is extremely large in this system, J~135meV;\textsuperscript{2} this unusually large exchange energy has encouraged many physicists to explore models of the superconductivity which involve 2-D magnetic effects. On the other hand, the magnetic coupling between CuO$_2$ layers is weak,\textsuperscript{1} and the 3-D order is actually a parasitic effect. Not surprisingly, undoped La$_2$CuO$_4$ exhibits 2-D antiferromagnetic correlations above the 3-D Néel transition; neutron scattering experiments indicate that the 2-D spin system is rapidly fluctuating, though strongly correlated.\textsuperscript{3} Some physicists have speculated that the rapid spin fluctuations are related to the quantum S = ½ nature of the spins; chapter 6 of this thesis will examine the spin dynamics of La$_2$CuO$_4$ in detail.

In doped samples, the 3-D antiferromagnetism is destroyed\textsuperscript{4} for hole concentrations greater than ~0.02 (see figure 2.1); magnetic correlations nonetheless persist in samples with no 3-D Néel transition. Muon spin resonance\textsuperscript{5} and nuclear magnetic resonance\textsuperscript{6} experiments have demonstrated that a spin glass-like transition occurs at low temperatures (T < 15K) in samples with no long range 3-D order, even in superconducting samples. Additional evidence that magnetism persists in the

\textbf{References}

\begin{itemize}
\end{itemize}
superconducting state may be found in the specific heat measurements of Gutsiedl et al.\textsuperscript{1} The most important aspect of the magnetism in metallic and superconducting La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4-y} is the nature of the spin correlations; this information can only be obtained from neutron scattering experiments. Chapter 7 of this thesis will examine the magnetic correlations found in La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4-y}, and a discussion of the relationship between the experimentally observed magnetic behavior and the superconductivity is given in chapter 8.

2.4 Superconducting Properties

Since a different mechanism is causing the superconductivity in the high-$T_c$ and conventional superconductors, it should not be surprising that many of the properties of the superconducting state are drastically different in the new materials. In this section a review of some of the measurements which have probed the superconducting properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ will be given.

One of the most basic questions is what the magnitude of $q^*$, the charge of the superconducting carriers, is. Early in 1987, Esteve et al.\textsuperscript{1} performed inverse AC Josephson effect measurements to resolve this issue. In these experiments a sample is irradiated with microwaves that have energy $\hbar \nu$, which causes steps in current versus voltage curves which are multiples of $\hbar \nu/q^*$ to appear. It was found that $q^* = 2e$, so that pairs of holes are carrying the current.

The superconducting coherence length, $\xi_S$, can be determined from measurements of $H_{C2}$; this measurement is somewhat complicated because of unusual flux lattice melting effects, though.\textsuperscript{2} Values for $\xi_S$ accurate to within a factor of two are 15Å within the CuO$_2$ planes, and 3Å perpendicular to the CuO$_2$ planes.\textsuperscript{2} In conventional superconductors, $\xi_S$ is typically greater than 100Å; the coherence length in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ is both small and anisotropic. Application of the Ginzburg criterion using these values for $\xi_S$ suggests\textsuperscript{3} that mean field theories of the

---

superconducting transition will not describe the behavior near $T_c$ accurately.

Unfortunately, no experimental consensus on the value of the superconducting quasiparticle excitation gap has been reached, yet. Values for the low temperature value of this quantity range from the weak-coupling BCS value of $3.5k_B T_c$ up to $\sim 7k_B T_c$. One explanation for this wide variation in reported values may be that the gap is anisotropic.\(^1\) Whether or not nodes exist in the gap is also controversial.\(^2\)

The isotope effect was one of the most important experimental clues in deducing that the superconductivity in conventional superconductors is related to phonons; consequently experiments which looked for this effect were done soon after the high-$T_c$ materials were discovered. An isotope effect was found in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system,\(^3\) which suggests that the motion of the ions does affect the superconductivity. However, the isotope effect in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is very small,\(^4\) so the role of ion motion is probably secondary to other effects.

---

2.5 Spectroscopic Studies

One of the main issues of high-$T_c$ research has been the nature of the electronic states involved with the superconductivity. Questions such as whether the Cu$^{2+}$ magnetic moments are predominately localized on their copper sites or are itinerant, which orbitals or bands do the doped in holes occupy, and what the magnitudes of the electronic correlation energies are can be at least partially answered from spectroscopic studies.

The nature of the Cu$^{2+}$ magnetic moments has been addressed in the work of Tranquada et al. In these measurements, the electronic valence state of the copper ions was monitored as the hole concentration was increased. It was found that all copper ions stay in the +2 valence state, regardless of the hole concentration. Two important conclusions can be drawn from this study. First, any magnetism which exists in La$_{2-x}$Sr$_x$CuO$_4$ is probably of a localized rather than itinerant nature. Second, the superconducting carriers must reside in bands which do not involve copper ions for the most part.

So which orbitals do the hole charge carriers go into? A partial answer to this question has been provided by Nücker et al., who found that the holes go into orbitals of predominately oxygen character. That the holes go on oxygen sites is unusual, since in almost all other materials the valence of oxygen is $-2$. This phenomenon appears to be an important clue about the nature of the high temperature

superconductivity.

Finally, it should be mentioned that spectroscopic studies can determine with reasonable accuracy values for the electronic correlation energies, overlap integrals, etc. that are in the Hubbard Hamiltonians discussed in the next chapter. The primary reference for this work is Shen et al.\textsuperscript{1}

\begin{enumerate}
\end{enumerate}
3. Theoretical Models of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$

In this chapter some of the models and ideas that have been used to describe the electronic behavior of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ will be discussed. One-electron, single-band Hubbard, and two-band Hubbard models in particular will be considered in sections 3.1, 3.2 and 3.3 respectively. All three of these approaches can explain the overall features of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system, such as the antiferromagnetism, the two dimensional behavior, and the insulator-metal transition. However, detailed predictions of the models are not always in agreement with experiment; the problems with each approach will be examined, and some of the key experimental results which must be accounted for will be discussed. In section 3.4, the effects of static disorder, which is not included in the vast majority of current theoretical work, will be reviewed. Finally, in section 3.5 specific models of the superconductivity which have been proposed will be examined.
3.1 One-electron Models

A good place to start when modeling the electronic structure of any system is with one-electron calculations. This is because the results of these calculations are easy to understand, and because other models of the electronic structure use the one-electron results as input.

The fundamental Hamiltonian to be considered is,

\[ H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2M_i} + \frac{1}{2} \sum_{<ij>} \frac{Z_i Z_j e^2}{|R_i - R_j|} - \sum_k \frac{\hbar^2 \nabla_k^2}{2m_e} + \frac{e^2}{2} \sum_{<kl>} \frac{1}{|R_k - R_l|} - \sum_{i,k} \frac{Z_i e^2}{|R_i - r_k|}, \] \hspace{1cm} (3-1)

Here the nuclear positions are given by \((R_i, R_j)\) and the electron positions by \((r_k, r_l)\), \(Z_i\) is the nuclear charge at site \(i\), and \((M_i, m_e)\) are the masses of the nuclei and electrons respectively. There are a number of simplifications which must be made in order to solve the problem. First, only the electrons in the outermost shells of the ions will determine most of the properties, so the core level electrons can be lumped together with their respective nuclei and then ignored. Second, the terms involving only the ions can initially be ignored, since the ions move much more slowly than the electrons. This is the famous Born-Oppenheimer approximation.

One-electron calculations include one additional approximation; this is that the electron-electron interaction term can be replaced by a mean field potential. For example, in the Hartree approximation the electron-electron potential seen by the \(k^{th}\) electron is approximated by

\[ V_k(r_k) = \sum_{l \neq i} \frac{e^2 |\psi_l(r_l)|^2}{|r_k - r_l|} dr_l \] \hspace{1cm} (3-2)

where \(\psi_l(r_l)\) is the wavefunction for the \(l^{th}\) electron. The Schrödinger equation for the
N-electron system can then be separated into N equations, the solutions to which are the one-electron wavefunctions. The important point is that the electron-electron interaction has been treated only in a mean-field sense in equation 3-2, which is an approximation made in all one-electron calculations. It turns out that this assumption causes some of the one-electron results on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ to be incorrect; one-electron calculations are nonetheless a useful first approximation for describing the electronic behavior.

Early in 1987, Mattheiss\textsuperscript{1} published a one-electron calculation of the electronic structure of $\text{La}_2\text{CuO}_4$. The results for the energy dispersion of the one-electron bands in selected high symmetry directions are shown in figure 3.1.

![Figure 3.1. One-electron Band Structure of $\text{La}_2\text{CuO}_4$.](image)

The seventeen band complex that is centered $-3\text{eV}$ below the Fermi level consists primarily of oxygen 2p and copper 3d states. The unoccupied bands $2\text{eV}$ above $E_F$

derive from La orbitals. Mattheiss suggested that only two of the seventeen bands in the Cu(3d)-O(2p) complex are important. These bands, labeled A and B in figure 3.1, are two dimensional in character since they arise from strong nearest neighbor interactions between the Cu–3d and O–2p orbitals shown in figure 3.2.

![Figure 3.2. Orbitals at E_F in the One-electron Band Structure](image)

The A or antibonding band shown in figure 3.1 is half filled, and it is essentially the only band at the Fermi level; La_2CuO_4 should therefore be a metal, according to the one-electron picture. This is a rather glaring discrepancy with experiment, since the data of figure 2.5 show that La_2CuO_4 is an insulator. There are two approaches that have been used to explain the insulating behavior. (i) A refinement of the basic one-electron approach can be applied, with the result that either a spin density wave (SDW) or charge density wave (CDW) causes the insulating behavior. (ii) The discrepancy between one-electron theory and experiment can be taken as a signal that the electron-electron interactions which were taken into account only in a mean field approximation must be treated differently; this is the viewpoint of the Hubbard model approaches discussed in sections 3.2 and 3.3.
The SDW-CDW approach to explaining the insulating character of La$_2$CuO$_4$ derives from the character of the two dimensional Fermi surface, which is shown in figure 3.3.

![Diagram](image)

**Figure 3.3.** 2-D Fermi Surface of La$_2$CuO$_4$

The interesting feature is that the square hole surface centered at the X-point in the Brillouin zone nests nearly perfectly with its electron counterpart centered at Γ. This suggests that either a charge density wave (CDW) or spin density wave (SDW) with $\bar{q} = 2k_F$ could open up a band gap at $E_f$, and make La$_2$CuO$_4$ insulating.

It was suggested$^1$ early in 1987 that the orthorhombic distortion could be the CDW causing the insulating behavior in La$_2$CuO$_4$. This is wrong, since La$_2$CuO$_4$ remains insulating in the tetragonal phase. The other possibility is that an SDW has formed; this scenario has been considered seriously by some physicists.$^2$

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antiferromagnetism is present in La$_2$CuO$_4$. There are a number of experimental results which cannot be explained by this approach, however. First, spectroscopic studies of the electronic structure, particularly those of Tranquada et al.,$^1$ suggest that the copper ions are in a +2 valence state, regardless of the degree of hole doping. The implication is that the 3d$^9$ holes are localized on the copper sites rather than delocalized into extended states, as the one-electron calculations predict. Second, the magnitude of the insulating gap (1-2eV) is too large to be caused by magnetic effects, and it does not collapse when the magnetic correlations decrease. Third, the spin dynamics in nearly stoichiometric La$_2$CuO$_{4+y}$ can be accounted for quantitatively with full Cu$^{2+}$ moments coupled together by the Heisenberg spin Hamiltonian used to describe antiferromagnetism in Mott insulators. The experimental results which have substantiated the Mott insulator approach will be discussed in chapter 6.

To date, the lattice dynamics of La$_{2-x}$Sr$_x$CuO$_{4-y}$ have been addressed at a microscopic level only in one-electron calculations. An early calculation of this type was done by Weber,$^2$ who predicted that a soft phonon mode involving "breathing" motions of the in-plane oxygen atoms coupled very strongly to the conducting electrons, enough to produce superconducting transition temperatures up to 40K in a conventional BCS theory. The soft breathing mode was not found in subsequent neutron scattering experiments,$^3$ which indicated that Weber's prediction was incorrect. Further, the discovery of high–T$_c$ superconductors with transition temperatures up to

125K has led most physicists to abandon phonon based pairing schemes of the superconductivity in the new materials.
3.2 Single-Band Hubbard Models

Early in 1987, P. W. Anderson suggested that very strong electron-electron correlations were present in the high-$T_c$ superconductors, and that these correlations would produce localized magnetic moments which were central to his theory of the superconductivity, the RVB model.\(^1\) He based his theory on the simplest Hamiltonian which could incorporate strong electron correlations, the single-band Hubbard model. Since Anderson's original proposal, an enormous amount of theoretical work has been done on the single-band Hubbard model and extensions of it.

The central problem with one-electron calculations of the electronic structure is that they predict La\(_2\)CuO\(_4\) to be a metal. To see how the electron-electron correlations which were treated only in a mean field approximation in the one-electron approach can give rise to insulating behavior, consider a lattice of hydrogen atoms where the lattice spacing can be continuously varied.\(^2\) In the one-electron picture, this system will have a single 1s band which is half filled, and consequently it will be metallic regardless of the lattice spacing. Now imagine that the lattice constant of this array is increased; it is clear that if the lattice constant becomes large enough, the electrons will become localized on individual hydrogen atoms. The reason why is that when 2 electrons are on a single hydrogen atom there is a large correlation energy, arising from the Coulomb potential, which prevents double occupancy of a single hydrogen site. This extra correlation between electrons is what Hubbard models attempt to take

---

The Hamiltonian for the single band version of the Hubbard model is

$$H = -t \sum_{<i,j>} c_{i\sigma}^\dagger c_{i+j\sigma} + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow}.$$  \hspace{1cm} (3.3)

Here $c_{i\sigma}^\dagger$ and $c_{i\sigma}$ are operators which create and annihilate electrons (or holes) with spin $\sigma$ on site $i$, $n_{i\uparrow} = c_{i\uparrow}^\dagger c_{i\uparrow}$ is the number of electrons (holes) with spin up on site $i$, and $t$ and $U$ the bandwidth and correlation energies respectively. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ it is more convenient to think of the incipient carriers as holes. The first term then represents the kinetic energy of the holes. Qualitatively, it takes into account the fact that the kinetic energy of a hole will be higher if it is confined to a single site. Thus a reduction in kinetic energy will occur through this term if the hole can hop to nearest neighbor sites. The second term represents the correlation energy which occurs from the double occupation of a site. The Pauli exclusion principal is built into this term because by definition no site can be doubly occupied by holes with parallel spins.

It is not universally accepted that the single band Hubbard model is a valid starting point to describe the superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$. It is therefore useful to describe what is left out in this approximation. Returning to the the one-electron calculations of Mattheiss, the band at the Fermi level was found to be derived from the $\text{Cu}(d_{x^2-y^2})-\text{O}(2p_{\sigma})$ orbitals shown in figure 3.2. In the single-band Hubbard model approach, the Cu–O band of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ is equated to the 1s band of the hydrogen lattice discussed above. Thus each CuO$_2$ unit is assumed to have states for 2 holes, one with spin up and the other with spin down. Now this is an enormous simplification of the problem, and a number of objections can be made about its
validity. For example, the inverse photoemission experiments of Nücker et al.\textsuperscript{1} indicated that the doped holes reside primarily on oxygen sites, so that a model with bands derived from both the copper and the oxygen orbitals would seem more appropriate. The photoemission experiments done by Shen et al.\textsuperscript{2} and others also favor a two-band model. Further, \textit{ab initio} calculations of the electronic structure which start from the fully correlated ionic limit\textsuperscript{3-6} have indicated that two-band models are more realistic. It is not obvious that the doped holes, which go primarily onto oxygen sites,\textsuperscript{1} actually form spin singlet states with the holes localized on copper sites analogous to the doubly occupied 1s orbitals of the hydrogen lattice. The system appears to be too complex for such a simple thing to happen.

With all these objections to the single band approach, it may seem strange that it is still being considered at all. The primary reason is that it is a far simpler model than any of the alternatives. The idea is to find the simplest effective Hamiltonian which has the correct symmetry of the problem, and solve this effective Hamiltonian to obtain the essential behavior. An analogous procedure is used to study many other systems; for example, the Ising model does not describe all aspects of real magnetic systems, but it is useful for describing many aspects of the critical behavior in some materials because it contains the essential symmetry. The objections raised against the single band approaches challenge whether these models have the correct symmetry of

\begin{itemize}
\end{itemize}
the system, that is, whether the fixed point is that corresponding to the one band models. There is currently no clear evidence which either favors or disfavors the one band approach.

A qualitative explanation of some of the behavior found in $La_{2-x}Sr_xCuO_{4-y}$ will now be given within the context of a single band Hubbard model. One of the most important features of $La_{2-x}Sr_xCuO_{4-y}$ which must be explained is why the stoichiometric system is an insulator. Hubbard model approaches explain this phenomenon quite naturally; the incipient hole carriers are primarily localized on copper sites so that the conductivity is reduced. This can also be seen in the representation of the density of states for this model shown in figure 3.4.

![Figure 3.4. Schematic Density of States in the Single-Band Hubbard Model](image)

The single Cu(3d)–O(2p) band splits into two bands, a lower band where the sites are singly occupied, and an upper band where the sites are doubly occupied. The average separation between the upper and lower Hubbard bands is $U$, and the width of the bands is $\sim 8t$. In $La_2CuO_4$, it is now widely believed that $U \gg t$ so the upper and lower bands do not overlap. Stoichiometric $La_2CuO_4$ is therefore an insulator, since
all bands are either empty or full.

Antiferromagnetism is expected in the $U/t \gg 1$ limit of the Hubbard model. Physically, the effect occurs because the antiferromagnetic spin configuration minimizes the kinetic energy of the holes. This can be seen by considering the 2-D ferromagnetic and antiferromagnetic clusters of spins shown in figure 3.5.

\begin{center}
\begin{tabular}{|c|c|}
\hline
ferromagnetic & antiferromagnetic \\
\hline
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{|c|c|}
\hline
\begin{tabular}{c}
\large $\uparrow$
\end{tabular} & \begin{tabular}{c}
\large $\uparrow$
\end{tabular} \\
\hline
\begin{tabular}{c}
\large $\uparrow$
\end{tabular} & \begin{tabular}{c}
\large $\uparrow$
\end{tabular} \\
\hline
\begin{tabular}{c}
\large $\uparrow$
\end{tabular}
\end{tabular}
\end{center}

\hspace{1cm}

\textbf{Figure 3.5.} Ferromagnetic and Antiferromagnetic Spin Clusters

In the ferromagnetic cluster, the central hole wavefunction cannot include states from any nearest neighbor sites, because the exclusion principle rigorously prevents any site from being doubly occupied with parallel spins. The kinetic energy of this hole is therefore increased because it is effectively confined to a smaller volume. On the other hand, in the antiferromagnetic spin configuration the central hole wavefunction can include states from neighboring sites, so that the kinetic energy is decreased. These ideas can be made quantitative by calculating the energy of the central hole in the ferromagnetic and antiferromagnetic spin configurations. In the ferromagnetic state the wavefunction of this hole is $|\Psi> = 10\uparrow>$, and the energy of this state is by definition 0. In the antiferromagnetic spin configuration, the wavefunction of the central hole
may be written as

$$|\Psi\rangle = 10^\uparrow + A \sum_{i=1}^{4} |i^\uparrow\rangle \tag{3-4}$$

where A is a parameter to be determined by minimizing the energy of the hole. This energy is

$$<\Psi | H | \Psi> = <0^\uparrow | H | 10^\uparrow> + 2A\sum_{i} <0^\uparrow | H | i^\uparrow> + A^2 \sum_{i,i'} <i^\uparrow | H | i'^\uparrow>. \tag{3-5}$$

Here $<0^\uparrow | H | i^\uparrow>$ is just the overlap integral t and $<i^\uparrow | H | i'^\uparrow>$ is the Coulomb energy U if $i = i'$. The energy of this variational state is then $E = 8At + A^2 4U$, which after minimizing gives $A = -t/U$ and $E_{AF} = -4t^2/U$. This is to be compared with the ferromagnetic state energy, $E_F = 0$. In order to take into account this difference between the antiferromagnetic and ferromagnetic energies, an effective spin Hamiltonian may be written. For this particular case,

$$H_{spin} = \frac{t^2}{U} \sum_{\langle i,j \rangle} \hat{s}_i^z \cdot \hat{s}_j^z = J \sum_{\langle i,j \rangle} \hat{s}_i^z \cdot \hat{s}_j^z, \tag{3-6}$$

which is the famous Heisenberg spin Hamiltonian. Much of the work presented in chapter 6 of this thesis will be devoted to comparing this model of the antiferromagnetism to the actual 2-D antiferromagnetism present in La$_2$CuO$_4$.

The motion of additional hole carriers drastically changes the character of antiferromagnetically ordered spin systems. When a hole moves, the Pauli exclusion principle allows a hop to another site only if the spin of the moving carrier is opposite to that of the hole on the final site. Consequently the motion of a hole carrier via nearest neighbor hops produces a string of flipped spins. This phenomenon is illustrated in figure 3.6.
Figure 3.6. Hole Motion in a Single-Band Hubbard Model

The spin flip processes break magnetic bonds, which increases the energy of the system and restricts the motion of the hole.\(^1\) Further, the spin lattice becomes disordered. Detailed calculations\(^2\) indicate that quantum fluctuations associated with the transverse exchange interaction cause spin flips which can repair the trail of flipped spins left by a moving hole, so that long range hole motion is possible. However, the width of the band corresponding to coherent hole motion is reduced from order \(t\) (\(-1\text{eV}\)) to order \(J\) (\(-0.13\text{eV}\)), and the effective mass of the carrier is enhanced considerably. Physically, the carriers still move in a band with width of order \(t\), but this motion is restrained by the high energy of the broken antiferromagnetic bonds, and a cloud of disordered spins is created around the carrier. Long range motion of the carrier will be determined by the spin flip time; the carrier along with its cloud of disordered spins moves at the rate \(-J/h\).

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The arguments given above qualitatively explain why doping with holes destroys the antiferromagnetic order. However, the 2-D antiferromagnetic correlation length as a function of hole concentration is not quantitatively specified,\(^1\) and the experimentally observed\(^2\) spin glass-like ordering is not accounted for. Further, experiment\(^3\) indicates that the motion of the carriers is dominated not only by spin scattering effects, but also by the effects of static disorder.

It has become clear that the superconductivity found in the high-\(T_c\) superconductors cannot be modeled by the basic single-band Hubbard model alone. A number of extensions have consequently been invoked by physicists who favor the single-band approach. For example, Anderson and Zou have emphasized hole tunneling between copper oxide layers as a necessary extension to the basic single-band model,\(^4\) and Lee\(^5\) has added a next nearest neighbor hopping term to the Hamiltonian, so that the holes can move to next nearest neighbor sites and avoid the spin flip processes described above. Many physicists have also argued that two-band models are necessary to model the essential aspects of the system.

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3.3 Two-band Hubbard Models

As discussed in chapter 2, it has been shown experimentally that the magnetism in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y \) arises from holes predominately localized on Cu 3d\(^9\) orbitals, while the superconducting current is carried by holes which reside in a band derived primarily from oxygen orbitals.\(^1\) A realistic model of the system should then include at least two bands, one for the copper moments and the other for the superconducting carriers. Such a model was proposed in advance of the experiments which support it by Emery.\(^2\)

A typical two-band model Hamiltonian is (3-7)

\[
H = \epsilon_p \sum_{i,\sigma} n_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} + \epsilon_d \sum_{j,\sigma} n_{i,\sigma} c_{j,\sigma}^\dagger c_{j,\sigma} - t \sum_{l,\sigma} n_{i,\dagger} r n_{l,\dagger} r + U_p \sum_{i} n_{i,\uparrow} n_{i,\downarrow} + U_d \sum_{j} n_{j,\uparrow} n_{j,\downarrow} + V \sum_{l,\sigma} n_{l,\sigma} n_{l,\sigma}.
\]

Here \( c_{i,\sigma}^\dagger \) creates holes on oxygen or copper sites, \( n_{i,\dagger} = c_{i,\dagger}^\dagger c_{i,\dagger} \), and \( r \) is a vector connecting nearest neighbor oxygen and copper sites. The first two terms represent the energy needed to place a hole on either an oxygen p orbital or copper d orbital. Thus \( \epsilon_p - \epsilon_d \) represents the average energy difference between the copper d and oxygen p bands. In \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y \) \( \epsilon_p > \epsilon_d \), so that holes first go on the copper band; these are the 3d\(^9\) holes present in stoichiometric \( \text{La}_2\text{CuO}_4 \). The correlation energy which is most important in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y \) is the energy to transfer a hole from a copper site to an oxygen site, not the energy to transfer a hole from a copper site to another copper site, as it would be in a single-band Hubbard model.\(^3\) The band gap, \( \Delta \), is therefore

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\( \epsilon_p - \epsilon_d + \delta \), where \( \delta \) is a correction term involving the band widths. The next term in the two-band Hamiltonian represents the kinetic energy gain which will occur if holes can wander on to neighboring sites; this term is therefore analogous to the \( t \) term in the single band Hubbard model. Note however that it represents the kinetic energy gained for holes wandering onto neighboring oxygen sites, not neighboring copper sites. The \( U_d \) and \( U_p \) terms represent Coulomb correlation energies from the double occupancy of oxygen and copper sites respectively; they are analogous to the Hubbard \( U \) of the single band model. Finally, the \( V \) term represents extra Coulomb energy which will arise if holes are on adjacent oxygen and copper sites.

The symmetry of the copper orbital in which the moments predominately reside is now generally believed to be \( 3d_{x^2-y^2} \). The symmetry of the oxygen orbitals in which the carriers predominately reside is still controversial; in figure 3.7 the two most likely oxygen orbitals are shown.

![Oxygen Orbitals](image)

**Figure 3.7. Oxygen Orbitals**

Most physicists prefer the \( 2p_\sigma \) orbital but there are currently no convincing theoretical arguments or experiments which have established the symmetry of the hole carrying
orbital. Clearly this matter will be crucial to the physics of the system, since the oxygen holes will interact in different ways with the copper moments depending on the symmetry of the orbital in which they reside. Table 3.1 and equation 3-8 below were derived assuming that the holes go into $p_\sigma$ orbitals; if the holes actually go into $p_\pi$ orbitals these results must be modified.

The two-band model can exhibit a large variety of phenomenon, depending on the values of $\varepsilon_p$, $\varepsilon_d$, $U_p$, $U_d$, $t$ and $V$. In table 3.1 approximate values for these parameters in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, as determined from recent ab initio calculations,\(^1\) are listed.

**TABLE 3.1. Parameter Values for the Two-Band Hubbard Model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_p - \varepsilon_d$</td>
<td>3.6</td>
</tr>
<tr>
<td>$t$</td>
<td>1.3</td>
</tr>
<tr>
<td>$U_d$</td>
<td>10.5</td>
</tr>
<tr>
<td>$U_p$</td>
<td>4.0</td>
</tr>
<tr>
<td>$V$</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Some insight into the physics of two-band models can be obtained by considering the density of electron states, given the parameters in table 3.1. A schematic representation might look as follows.

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Figure 3.8. Schematic Density of States in the Two-Band Hubbard model

The density of states shown here is similar to the one-band model density of states shown in figure 3.4, except that the Fermi level lies between a copper $3d^{10}$ band and oxygen $2p^6$ band instead of bands which formally represent singly and doubly occupied Cu–O hybrid states. Thus the two-band model accounts for the insulating behavior in $\text{La}_2\text{CuO}_4$ in a manner similar to the one-band approach. The two-band approach can also account for the antiferromagnetism seen in $\text{La}_2\text{CuO}_4$. If the spin configuration is antiferromagnetic, the holes from neighboring copper sites can both wander onto the oxygen between them, while if the spin configuration is ferromagnetic they cannot. Thus the kinetic energy of the holes is lower in the antiferromagnetic than in the ferromagnetic state. A derivation of the exchange constant is similar to the derivation presented above for the single band model, though more complicated. Emery and Reiter\textsuperscript{1} find the exchange to be

\begin{tabular}{l}
\end{tabular}
\[ J = \frac{4t^4}{(\varepsilon_p - \varepsilon_d + V)^2} \left( \frac{1}{U_d} + \frac{2}{U_p + 2(\varepsilon_p - \varepsilon_d)} \right). \] (3-8)

Some aspects of the two-band model with extra hole carriers will now be discussed. Consider the situation illustrated in figure 3.9,\(^1\) where a doped in hole is localized on a single oxygen site, and the copper spins are assumed to be classical for computational convenience.

![Diagram of magnetic frustration](image)

Figure 3.9. Hole Induced Magnetic Frustration

The oxygen hole will disturb the antiferromagnetic coupling of the neighboring copper moments for at least two reasons. First, the presence of the hole on the oxygen orbital affects the motion of the holes on neighboring copper sites. Second, direct exchange between the hole on the oxygen atom and the holes on the copper atoms will favor a ferromagnetic alignment of the copper spins, regardless of the sign of the direct exchange. The net result is that the Cu–Cu magnetic bond becomes ferromagnetic,

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which leads to some interesting effects. In figure 3.9 it can be seen that the ferromagnetic bond has caused the copper moments around it to go into a spiral type structure, which gives some indication about the type of spin order which may be present in doped La$_{2-x}$Sr$_x$CuO$_{4-y}$. Further, the frustration caused by the ferromagnetic bond can cause spin glass behavior.\footnote{Mattis, D. C., Theory of Magnetism II, (Springer-Verlag, 1985).} As mentioned in chapter 2, spin glass-like behavior has been observed in La$_{2-x}$Sr$_x$CuO$_{4-y}$; it should be noted that only the two-band model described here has explained this behavior. Moreover, there is some evidence\footnote{Harshman, D. R., et al., Phys. Rev. B 38, 852 (1988)} that the actual spin glass transition observed in La$_{2-x}$Sr$_x$CuO$_{4-y}$ occurs only after some of the hole carriers have become localized, which is consistent with the assumptions of this model.

Hole carriers can move in a number of different ways in a two-band model. If the carriers go into oxygen $p_\pi$ orbitals,\footnote{Birgeneau, R. J., Kastner, M. A., Aharony, A., Z. Phys. B 71, 57 (1988).} they could hop directly to neighboring oxygen sites without causing spin flips in the copper moments. The carriers would then behave in many ways like free carriers. If the carriers go into $p_\sigma$ orbitals, more complicated interactions with the copper moments will occur as the hole carrier moves. Emery and Reiter\footnote{Emery, V. J., Reiter, G., Phys. Rev. B 38, 4547 (1988).} have argued that the doped holes form singlets with copper holes analogous to the singlets of the one-band models. These singlets are more complicated than the one-band model singlets, though, and no simple picture equivalent to figure 3.5 has emerged to describe the effect that mobile holes have on the Cu moments; in fact, Emery and Reiter do not address the issue.
3.4 Static Disorder

The $La_{2-x}Sr_xCuO_{4-y}$ system must, by virtue of its nonstoichiometric composition, exhibit some degree of static disorder. The models described in the previous 3 sections have not taken into account the effects of this disorder; in this section some of the ideas used to describe it will be discussed.

The conductivity of lightly doped ($p<0.01$) $La_2CuO_{4+y}$ will be considered first. Because of the oxygen defects present, the potential seen by the hole carriers is not periodic; instead, there are randomly spaced, deep potential wells near the $O_2^{1-}$ acceptor sites which will tend to trap the carriers. If all states at the Fermi level are localized around the traps, then the carriers will only be able to hop between trap sites. The hopping rate between two localized sites is of the form\(^1\)

$$v \sim v_0 e^{-w/k_BT} e^{-2\alpha R}.$$ (3-9)

Here $w$ is the energy difference between the trap sites, $R$ is their separation, and $1/\alpha$ the extent of the localized electronic wavefunction associated with the traps. $v_0$ is an attempt frequency; since phonons usually supply the energy necessary for the hopping process to occur, $v_0$ is of the order of tens of meV. In a typical hopping process, a carrier just below the Fermi level jumps to a state just above it. The farther the carrier jumps, the greater the choice of states that it has, and in general a smaller value for $w$ will attained. On the other hand, if the states are separated by too large of a distance, the $e^{-2\alpha R}$ factor will suppress the hopping process altogether. If a carrier

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jumps a distance $R$, then on the average the energy difference between the two sites is

$$w = \left( \frac{4\pi}{3} R^3 g(E) \right)^{-1}$$  \hspace{1cm} (3-10)

where $g(E)$ is the density of states at the Fermi level. Using equation 3-10, one can maximize the hopping rate with respect to $R$ to find the optimum hopping distance. It turns out that this distance is given by $R_m = (\alpha k_B T g(E))^{-1/4}$, which leads to a hopping conductivity of the form

$$\rho = \rho_0 \exp(\frac{T}{T_0})^{-1/4}.$$  \hspace{1cm} (3-11)

This is the famous Mott $T^{-1/4}$ variable range hopping law. As discussed in chapter 2, the resistivity of $\text{La}_2\text{CuO}_{4+y}$ samples roughly follow this form, which indicates that the states at the Fermi level are localized.

A plausible modification of the density of states of the two-band Hubbard model to include the effects of static disorder might look like figure 3.10.
This basic scenario was described in the work of Preyer et al.\textsuperscript{1} An impurity band arising from acceptor states lies between the upper and lower Hubbard bands, and the Fermi level lies within this impurity band in lightly doped (p<0.01) samples. Further, the states in the impurity band are localized, so that hopping conductivity is observed at low temperatures. At high temperatures, the conductivity has an activated temperature dependence, \( \sigma = \sigma_0 \exp(-E_0/k_BT) \), which occurs because the majority of the carriers are then holes in the lower Hubbard band of figure 3.10. The activation energy for these carriers, \( E_0 \), is the energy difference between the impurity band and the lower Hubbard band. It should be mentioned that although the scenario described above seems to agree with all current experimental information, other explanations are

also possible.

The actual insulator transition which occurs in $\text{La}_2\text{CuO}_{4+y}$ will now be addressed. When the concentration of hole carriers is increased, the overlap between the localized states will increase, and the system will become metallic when $E_F$ first lies in a region where the electronic states are extended. This type of insulator-metal transition is called an Anderson transition. A simple argument due to Mott gives a reasonable prediction of the carrier concentration at which an Anderson transition occurs. If the carriers are considered to be bound to the acceptor sites in Bohr orbits, then their orbital radius is $r_0 = \hbar^2 \varepsilon / m^* e^2$ where $\varepsilon$ is the dielectric constant. On the other hand, the Thomas-Fermi screening length is $\lambda^2 = \hbar^2 \varepsilon / 4 m^* e^2 (3 n_3 / \pi)^{1/3}$ where $n_3$ is the 3-D carrier concentration. Mott argued that the carriers will no longer be bound to the trap sites when $r_0 = \lambda$; this leads to a relation between the critical carrier concentration and the Bohr radius of the material, $(n_3)^{1/3} r_0 = 0.25$. Note that this argument applies to a 3-D insulator-metal transition; similar arguments$^1$ have been made for 2-D systems, with the result that $(n_2)^{1/2} r_0 = 0.15$. Experimentally, the Anderson transition occurs in $\text{La}_2\text{CuO}_{4+y}$ at a hole concentration of $-5 \times 10^{19}/\text{cm}^3$ ($p \sim 0.01$) and the localization length is $\sim 8\text{Å}$,$^2$ which is consistent with both the 3-D and 2-D Mott criteria.

In a two dimensional system, even after the Anderson transition has occurred the resistivity of the system does not resemble that of a typical metal. This can be seen

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most directly using the Feynman path integral formulation of quantum mechanics. When a carrier moves, the amplitude for propagation between two points is given by the sum of the classical amplitudes over all paths connecting the points. For a free carrier, the dominant paths lie in a straight tube connecting the end points. For carriers which move in a disordered system, scattering from impurities will produce several dominant trajectories which lie in haphazard directions. The phases for most of the trajectories are random, so that interference terms sum to zero and the carrier acts like a classical object. However, it turns out that for closed loop trajectories constructive interference occurs between the paths where the particle propagates in opposite directions. In 2-D systems this greatly enhances backscattering processes, which in turn causes the carriers to be effectively localized, even though the states at the Fermi level are extended. The presence of any disorder will cause this effect; it is therefore known as weak localization. The decrease in the conductance of a system which results from weak localization effects takes the form

\[ \Delta G = \frac{e^2}{\pi h} \ln(T). \]  

(3-12)

This result holds only when the change in conductance due to weak localization effects is much smaller than the conductance itself.

When a magnetic field is applied to a localized 2-D metal, all Feynman paths pick up the extra phase factor \( \int A^z \cdot dl \), where \( A^z \) is the vector potential. Consequently a closed loop trajectory and its conjugate will pick up opposite phases, and the weak

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localization effects will be destroyed when the phase difference for the typical loop is of order $\pi$.\(^1\) It turns out that the average loop area is determined by the length scale of dephasing inelastic collisions; consequently the resistivity will increase when $BL \approx \Phi_0 \approx h/e$. Estimates of the inelastic scattering length can therefore be found from magnetoresistivity measurements. In samples of La$_{2-x}$Sr$_x$CuO$_{4-y}$ which are near the superconductivity threshold, this length appears\(^2\) to be greater than $\sim 500\text{Å}$. Work is currently being done to test other aspects of weak localization theory in the La$_{2-x}$Sr$_x$CuO$_4$ system.\(^3\)

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1. The copper moments in La$_{2-x}$Sr$_x$CuO$_4$ may modify some aspects of weak localization theory through $\int A \cdot \text{d}l$ terms.
2. Preyer, N. W., private communication.
3. Preyer, N. W., ongoing work.
3.5 Theories of High Temperature Superconductivity

The first thing that should be stated about the various theories of high temperature superconductivity which have been proposed is that that few of them have successfully predicted anything. This field has been dominated by experimental discoveries. It it nonetheless useful to discuss a few of the current high–T_c theories because some of the basic ideas found in some of them might eventually turn out to be correct.

The idea that charge fluctuations (excitons) can cause superconductivity was originally proposed in 1964 by Little. In this scheme, the superconducting carriers polarize an underlying lattice of electrons, much as the ionic lattice is polarized in conventional superconductors. Excitonic theories of the superconductivity in La_{2-x}Sr_xCuO_4-y have been proposed by Varma et al. and Weber; Little himself has also argued in their favor. One of the main predictions of the current excitonic high–T_c theories is that magnetic effects are not directly related to the primary interaction responsible for the superconductivity. The principal experimental evidence which favors excitonic as opposed to magnetic mechanisms therefore is that Ba_xK_{1-x}BiO_3 apparently does not exhibit any unusual magnetic properties. On the other hand, the experimental evidence presented in Shirane et al. and Thurston et al.

demonstrates that there is a direct connection between the magnetism and superconductivity in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \); thus all current excitonic theories of the superconductivity in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \) are at the minimum incomplete. A detailed description of the experimental evidence linking the superconductivity with magnetic interactions will be presented in chapter 7.

A theory which has stimulated much work on the magnetism found in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) is Anderson's RVB model.\(^1\) One of the basic ideas of the RVB model is that the \( S = \frac{1}{2} \) nature of the magnetic interactions in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \) produce quantum fluctuations which destroy Néel order. The quantum disordered state which Anderson envisaged, the RVB state, has all spins in the system paired in singlet states, so that the many body wavefunction also has spin 0. The distance between paired spins can be arbitrarily large, and the state "resonates" between different spin pairing configurations. A simple physical picture which might be analogous to the RVB state is a spin fluid. After the pioneering work of Shirane \textit{et al.}\(^2\) and Endoh \textit{et al.}\(^3\), Anderson identified\(^4\) the unusual 2-D spin state found above the 3-D Néel transition in \( \text{La}_2\text{CuO}_4 \) with the RVB state. Subsequent work by Birgeneau \textit{et al.}\(^5\) and Yamada \textit{et al.}\(^6\) have shown that Anderson's proposal was incorrect. This issue will be discussed in chapter 6. In doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \), experimental work\(^5\) has shown that the spin

\(^{1}\text{Anderson, P. W., Science 235, 1196 (1987).}\)
\(^{5}\text{Birgeneau, R. J., \textit{et al.}, Phys. Rev. B 38, 6614 (1988).}\)
\(^{6}\text{Yamada, K., \textit{et al.}, accepted by Phys. Rev. B.}\)
system is highly disordered; thus the RVB model may still be relevant to the superconductivity. The theory is still not sufficiently well developed to make quantitative comparisons to experiment, however.

Superconductivity via hole pairing\(^1\) is occurring in La\(_{2-x}\)Sr\(_x\)CuO\(_4\); two simple ideas which suggest how this pairing happens will be discussed now. The first idea follows from figure 3.6, which showed that hole carriers leave a string of flipped spins as they move. Now if two holes move together, the second hole can reflip the spins overturned by the first hole, so that both holes become mobile.\(^2\) Thus hole pairing is related to antiferromagnetic order in the copper spin system. A number of objections can be made to this scheme for hole pairing. For example, this model assumes that reasonably long ranged antiferromagnetic spin correlations exist, while the experiments described in chapter 7 indicate that the actual spin state has only short ranged spin correlations. Further, the antiferromagnetic interactions which pair the holes are probably weaker than carrier-moment interactions which have been ignored. This example nonetheless provides a hint of how the holes might actually get paired in a strongly interacting antiferromagnet.

The second example of carrier pairing which will be considered is based on the magnetic frustration\(^3\) shown in figure 3.9. The magnetic frustration energy associated with the canting of copper spins surrounding two isolated holes can be shown to be

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greater than the magnetic energy of two holes which are separated by only a few lattice constants. The situation is summarized in figure 3.11.

![Diagram of hole pairing via magnetic frustration]

**Figure 3.11.** Hole Pairing via Magnetic Frustration

The canting fields of the isolated holes are largely cancelled when the holes are brought together. This produces a pairing mechanism which depends strongly on the configuration of the copper moments.

No completely successful theory of the superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ has been devised, yet. In short, there are just too many ways in which the spins and the carriers can produce a superconducting ground state, so that no single theory has been proven to be the correct description. Concrete experimental facts are needed to guide physicists to the correct description of this strongly correlated electronic state.
4. Experimental Details

Some of the scattering techniques and preliminary experimental work will be described in this chapter. In sections 4.1 and 4.2 the magnetic and nuclear neutron scattering cross-sections are reviewed. Details of the neutron scattering technique are discussed in section 4.3, and in section 4.4 crystal growth procedures and sample characterization measurements are presented.
4.1 Magnetic Neutron Scattering Cross-sections

Thermal neutrons are perhaps the ideal probe of condensed matter excitations. The wavelengths of thermal neutrons are comparable to the interatomic distances in solids and the energies of thermal neutrons are of the order of both phonon and magnon energies. The disadvantage of neutron scattering is that the flux of thermal neutrons at even the best sources is small compared to the photon flux of lasers and synchrotron x-ray sources.

A schematic diagram of a typical neutron diffraction spectrometer is shown in figure 4.1.

![Diagram of a neutron diffraction spectrometer]

**Figure 4.1. Triple Axis Spectrometer**

The name "triple axis" derives from the fact that neutrons are diffracted off three crystals, the monochromator, the sample and the analyzer. Bragg reflection from the monochromator provides a neutron beam with a single energy $E_i$ and momentum $\mathbf{P}_i$; Bragg reflection from the analyzer crystal determines the energy $E_f$ and momentum $\mathbf{P}_f$ of the detected neutrons. Thus the momentum transferred to the sample is
\[ Q' = R'_i - R'_f \] (4-1)

and the energy transferred is

\[ \omega = E_i - E_f \] (4-2)

The interactions between a neutron and the magnetic moment and nucleus of an individual atom are discussed in, for example, the book by Marshall and Lovesey.\(^1\)

This thesis deals with the spatial and temporal correlations of spins or nuclei in a condensed matter system which can be measured through coherent neutron scattering techniques. Consequently only those aspects of the cross-sections relevant to the measurement of correlation functions will be discussed here. The scattering cross-sections for magnetic and lattice excitations are similar in many respects. However, in systems such as La\(_2\)CuO\(_4\) which have many atoms in a unit cell, the magnetic excitations are easier to visualize than the lattice excitations. For this reason, the magnetic scattering cross-section will be reviewed more extensively than the phonon cross-section.

The cross-section for spin only scattering within solid angle \( d\Omega \) and energy interval \( dE_f \) is,\(^2\)

\[
\frac{d^2\sigma}{d\Omega dE_f} = \frac{(\gamma_0 g)^2}{8\pi} \frac{k_f}{k_i} f(Q')^2 \sum_\alpha (1 - \hat{Q}_\alpha^2) S'^{\alpha\alpha}(Q', \omega)
\] (4-3)

where

---

$$S^{\alpha\alpha}(Q', \omega) = \frac{1}{2\pi N} \int e^{i\omega t} <s^{\alpha}(-Q', 0)s^{\alpha}(Q', t)> dt. \quad (4-4)$$

Here $f(Q')$ is the magnetic form factor, $\alpha$ refers to the x, y, or z axes, $g$ is the Lande factor, $\vec{r}$ is a lattice vector, and $\gamma_0$ is a constant with numerical value $5.39 \times 10^{-13}$ cm. The $(1 - Q'^2)$ factor arises from the nature of the interaction between the dipole moment of the neutrons and the spins; it allows scattering only when $Q'$ is perpendicular to the direction of the spins. The quantity $S^{\alpha\alpha}(Q', \omega)$, known as the Van Hove scattering function, is the Fourier transform in both space and time of the spin-spin correlation function $<s^{\alpha}(Q', 0)s^{\alpha}(\vec{r}, t)>$. This quantity is a thermal average over the correlations between the components along the $\alpha^{th}$ axis of a spin at the origin at time zero and a spin at site $\vec{r}$ at time t.

The magnetic form factor, $f(Q')$, is the Fourier transform of the density of unpaired electrons in a single magnetic ion,

$$f(Q') = \int \rho_{ion}(\vec{r}) e^{iQ' \cdot \vec{r}} d\vec{r} \quad (4-5)$$

Freitoft et al.\(^1\) have measured the magnetic form factor for the Cu$^{2+}$ ions in La$_2$CuO$_4$; their results for $f(Q')$ are shown in figure 4.2.

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In almost all of the experiments discussed in this thesis, $Q$ is sufficiently small that the magnetic form factor may be regarded as a constant.

In order to illustrate some of the qualitative features of $S^{\alpha\alpha}(Q',\omega)$, a few examples will now be discussed. The simplest magnetic state possible is a spin lattice which is perfectly ordered along one axis; a classical Heisenberg magnet at $T = 0$ would be in such a state. If the spins are aligned along the $z$ axis the spin-spin correlation function is then $\langle s^2(0,0)s^2(\tau,0)\rangle = s^2$, and from equation 4-4 the scattering function is

$$S^{zz}(Q',\omega) \sim \delta(\omega) \left\{ \sum_{\tau} \delta(Q' - \tau) \right\}.$$  \hspace{1cm} (4-6)

The delta function in energy transfer causes the scattering to be elastic, $E_i = E_f$, and the delta functions in momentum transfer are at Bragg peak positions, $Q' = \tau$. If the spins are correlated in three dimensions, the Bragg peaks form points of scattering in momentum transfer space $(Q_x,Q_y,Q_z)$, while if the spins are correlated in only two dimensions rods of scattering are formed. This difference between the scattering in
two and three dimensionally correlated systems is actually observed in La$_2$CuO$_4$. In the 3-D Néel state, the spin structure shown in figure 2.6 leads to Bragg peaks at the orthorhombic reciprocal lattice positions shown in figure 4.3. Above the 3-D Néel transition, 2-D antiferromagnetic correlations within the CuO$_2$ planes produce scattering centered at, for example, the (1,k,0) and (0,k,1) rods.

![Graph showing reciprocal lattice positions](image)

**Figure 4.3.** Reciprocal Lattice of La$_2$CuO$_4$

The scattering from a system which has fluctuating spins is more complicated than when the spins are static. As an example, consider the scattering found in the paramagnetic state of a *classical* Heisenberg antiferromagnet. The scattering function for this case was calculated by Van Hove, who found that the delta functions of equation 4-6 are replaced by functions which are approximately Lorentzians,

\[
S^{xx}(Q',\omega) = -\frac{\Gamma}{\omega^2 + \Gamma^2} \left\{ \sum_{\tau} \frac{k_B T}{(Q' - \tau)^2 + \kappa^2} \right\}.
\]  

\[ (4-7) \]

---

The qualitative behavior of the spin correlations may be found by taking the inverse Fourier transform of equation 4-7. For convenience $\Gamma$ is assumed to be constant, though in fact it is usually a function of $|\mathbf{Q} - \mathbf{q}|$. This gives

$$<s^z(\mathbf{q},t)s^z(\mathbf{q}',t) >= e^{-\Gamma t} \frac{e^{-\kappa \mathbf{r}}}{r^{(d-1)/2}}$$

(4-8)

where $d$ is the dimension of the system. Equations 4-7 and 4-8 reveal many of the features of the scattering which are observed in real magnetic systems. Consider momentum transfer scans through a Bragg position, as in figure 4.4.

![Intensity vs. Q plots for large and small $\kappa$ and small and large $\xi$.](image)

**Figure 4.4. Momentum Transfer Scans**

The scan on the left is broad, so its half width at half maximum, $\kappa$, is large. From equation 4-8, the spin-spin correlation function is proportional to $e^{-\kappa r}$, which means that the size of correlated patches of spins is small when $\kappa$ is large. On the other hand, when $\kappa$ is small so that most of the scattering is concentrated around the Bragg

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position, the size of the correlated spin patches is large. Because of this relationship between $\kappa$ and the size of correlated spin patches, $1/\kappa$ is defined to be the magnetic correlation length $\xi$.

A similar argument holds for the energy distribution of the scattering.

![Graph showing energy transfer scans](image)

**Figure 4.5. Energy Transfer Scans**

When $\Gamma$ is large, much of the scattering intensity is inelastic, and from equation 4-8 the spins are rapidly fluctuating. When $\Gamma$ is small, the scattering is quasielastic and the spins are nearly static. As a magnetic system orders, the size of the correlated spin patches grows and the spins fluctuate less rapidly. Both of these effects can be measured in neutron scattering experiments, which will measure scattering which becomes sharp in both momentum and energy transfer as the system orders.

The one-magnon cross-section for the harmonic excitations found in an ordered Heisenberg antiferromagnet will be discussed now. Clearly this cross-section is relevant for neutron scattering measurements of the 3-D Neel state of $\text{La}_2\text{CuO}_4$; it is also a useful first approximation for describing the excitations in disordered
La$_{2-x}$Sr$_x$CuO$_{4-y}$: The one-magnon cross-section for a single mode is\(^1\)

\[
S(Q',\omega) = \left(\frac{1}{e^\omega q_k^T - 1} + 1\right) \delta(\omega(q') - \omega)\delta(q' - q - \tau) \frac{1}{\omega(q')} + \\
\left(\frac{1}{e^\omega q_k^T - 1}\right) \delta(\omega(q') + \omega)\delta(q' + q - \tau) \frac{1}{\omega(q')}
\] (4-9)

\[
S(Q',\omega) = \left(\frac{1}{e^\omega q_k^T - 1} + 1\right) \left[\frac{1}{\gamma^2 + (\omega - \omega(q'))^2}\right] \frac{1}{\omega(q')}
\]

\[
\left(\frac{1}{e^\omega q_k^T - 1}\right) \left[\frac{1}{\gamma^2 + (\omega + \omega(q'))^2}\right] \frac{1}{\omega(q')}
\]

The last line of equation 4-9 follows when the magnons have a finite lifetime, 1/\(\gamma\). The energy of the magnon, \(\omega(q')\), is given by

\[
\omega(q') = \sqrt{E_{\text{gap}}^2 + (vq)^2}
\] (4-10)

for small \(q\). In La$_2$CuO$_4$, neutron scattering experiments\(^2\) indicate that the velocity, \(v\), is about 800meVÅ and that the gaps present\(^3\) in the Néel state are about 1.9 and 2.5meV. The first term in equation 4-9 corresponds to processes where a neutron creates a magnon, and the second term corresponds to magnon annihilation processes. The delta functions insure that momentum and energy are conserved in the scattering process. In La$_2$CuO$_4$, the dispersion of the 2-D magnons would resemble the schematic diagram shown in figure 4.6.

---

Figure 4.6. Dispersion of 2-D Antiferromagnetic Magnons

Here the creation and annihilation processes have positive and negative $\omega$ respectively, and the orthorhombic $h$ and $l$ directions, which are perpendicular to the 2-D Bragg rods, correspond to the momentum axes. The "ice cream cone" structure shown in figure 4.6 is useful for understanding many of the magnetic measurements presented in this thesis; it will show up again.

Many of the scans which have been used to probe the $La_{2-x}Sr_xCuO_{4-y}$ system have been done so that an integration over energy transfer from $-k_BT$ to $E_i$ is performed automatically. A trick which can be applied only to systems which are correlated one or two-dimensionally is used to accomplish this integration. A description of the trick is given below; consider now what this type of scan measures:
\[ I(Q') = \int_{-k_BT}^{E_i} \frac{d^2\sigma}{d\Omega dE_i} d\omega \]

\[ I(Q') = \int_{-k_BT}^{E_i} d\omega \left| f(Q') \right|^2 k_{f} k_{i} \frac{1}{2\pi N} \int_{-\infty}^{+\infty} e^{i\omega t} <s(-Q',0)s(Q',t)> dt. \]

If most of the scattering intensity is well within the integration limits, then the limits may be changed to \( \pm \infty \). Further, the magnetic form factor and \( k_f/k_i \) will be approximately constant. Under these conditions, equation 4-11 simplifies to

\[ I(Q') \sim \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} e^{i\omega t} <s(-Q',0)s(Q',t)> dt \]

\[ I(Q') \sim \int_{-\infty}^{+\infty} \delta(t) <s(-Q',0)s(Q',t)> dt \]

\[ I(Q') \sim <s(-Q',0)s(Q',0)> \]

If the approximations in going from equation 4-11 to 4-12 are valid, the spatial Fourier transform of an instantaneous correlation function will be measured. In other words, a "snap shot" of the spin configuration is taken. A specific example of this type of scattering may be found by integrating equation 4-7 over energy transfer

\[ I(Q') \sim \int_{-\infty}^{+\infty} S^{zz}(Q',\omega) d\omega \]

\[ I(Q') = \sum_{\tau} \frac{k_{B}T}{(Q' - \tau^2 + \kappa^2} \]

The instantaneous scattering function for a classical Heisenberg paramagnet is just a Lorentzian. This is a convenient fitting function which describes most of the La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4-y} data well, consequently many of the scans presented in chapters 6 and 7 have been fit to this form.
The details of the energy integration trick will now be described. In this type of scan, the analyzer is removed so that all neutrons which are diffracted off the sample are detected; for this reason, it is also commonly called a 2-axis scan. The range of energy transfers which are integrated over is \(-k_B T\) to \(E_f\). The lower limit is the average amount of energy which a neutron can gain by destroying a thermally generated excitation, and the upper limit is the highest energy excitation which can be created by a neutron. This procedure cannot generally be done at a fixed momentum transfer, however, because \(E_f\) and \(k_f^2\) are coupled through the relation

\[
E_f = \frac{\hbar^2}{2m_N} k_f^2. \tag{4-14}
\]

This is where the two-dimensional nature of the system comes in. From equation 4-7, the relevant momentum transfer is not \(Q^r\), but \(Q^r - \tau\). In a system which is two-dimensionally correlated, \(Q^r - \tau\) is the perpendicular distance to a Bragg rod; thus if the scattering geometry is set up so that \(k_f^\prime\) is parallel to the Bragg rod, \(Q^r - \tau\) remains unchanged for all \(k_f^\prime\). This scattering geometry is illustrated in Figure 4.7.

---

The condition for $\mathbf{R}_f$ to be along the 2-D rod depends on $E_i$ and the perpendicular distance to the rod, $|Q^* - \bar{r}|$. In orthorhombic units, the rods of scattering found in La$_2$CuO$_4$ are along the $b^*$ direction ($b^* = 2\pi/b$); therefore if the momentum transfer is $Q^* = h\bar{a}^* + kb^*$, then the perpendicular distance to the Bragg rod is $|Q^* - \bar{r}| = ha^*$. Under these conditions, the position along the 2-D rod where $\mathbf{R}_f$ is parallel to $b^*$ is

$$kb^* = k_i - \sqrt{k_i^2 - (ha^*)^2} \quad (4-15)$$

At the two most commonly used incident neutron energies, $E_i = 14.7\text{meV}$ and $30.5\text{meV}$, $\mathbf{R}_f$ is parallel to $b^*$ at $(h = 1, k = 0.58)$ and $(h = 1, k = 0.39)$ respectively.

It is interesting to see the trajectory of a scan across the rod which has $\mathbf{R}_f$ parallel to $b^*$; such a scan with $E_i = 14.7\text{meV}$ is shown in figure 4.8.
Figure 4.8. 2-axis Scan Across the Rod

The unusual slant in the energy integrating 2-axis scan has mystified scores of theorists working in the high-$T_c$ field. Note that if the scattering in a system is both two-dimensional and highly inelastic, then a 2-axis scan up a Bragg rod position should peak when $K_f$ is parallel to the rod. As discussed in chapters 6 and 7, this effect is actually seen in $\text{La}_2-x\text{Sr}_x\text{CuO}_4-y$.

A variant of the standard 2-axis scan has been used extensively to remove parasitic background scattering. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, it turns out that most of the parasitic scattering arises from quasielastic $\omega \sim 0$ processes, while most of the intrinsic signal occurs at energies greater than $-0.5$ meV. This suggests that if the $\omega \sim 0$ scattering could somehow be removed, a much cleaner signal would result. A technique for removing the $\omega \sim 0$ scattering, the filtered 2-axis scan,\textsuperscript{1} will be discussed now. In the filtered 2-axis technique, the analyzer is set to diffract $\omega = 0$ neutrons,

and the detector is positioned to detect all neutrons which pass through the analyzer. Because most of the $\omega \sim 0$ neutrons are diffracted off the analyzer, they are not detected and the $\omega \sim 0$ parasitic scattering is partially removed. In practice, however, the reflectivity of the analyzer is not perfect. In order to correct for analyzer inefficiency, scans which detect the $\omega \sim 0$ diffracted neutrons and the neutrons which are transmitted through the analyzer are performed. The $\omega \sim 0$ scan may then be scaled by the analyzer reflectivity and subtracted from the transmission scan. The net result is a scan which shows only the inelastic signal.
4.2 Nuclear Neutron Scattering Cross-sections

The general cross-section for nuclear scattering is given by\(^1\)

\[
\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle F(-Q',0)F(Q',t)\rangle e^{iQ \cdot \mathbf{r}} dt
\]  

(4-16)

where \(F(Q',t)\) is defined by

\[
F(Q',t) = \sum_{j} b_j e^{iQ \cdot \mathbf{r}_j(t)}.
\]

(4-17)

The sum is over all atoms in the lattice and \(b_j\) is the coherent scattering length for the \(j\)th atom.

Rather than using these expressions directly, it is sufficient for the purposes of this thesis to consider only the two lowest order terms of an expansion of equation 4-16, the Bragg and one-phonon cross-sections. The Bragg cross-section is determined by the average positions of the atoms; it is therefore elastic and analogous to the spin cross-section given in equation 4-6. The one-phonon cross-section measures the harmonic fluctuations of the atomic positions; it is inelastic and somewhat analogous to the spin cross-section given in equation 4-7.

The coherent Bragg cross-section is given by

\[
\frac{d^2\sigma}{d\Omega dE_f} = N \frac{(2\pi)^3}{\nu_0} |F(Q')|^2 \delta(\omega) \sum \delta(Q' - \mathbf{q}).
\]

(4-18)

Here \(\nu_0\) is the volume of a unit cell, and the elastic structure factor is

---

\[ F(Q^*) = \sum_d b_d e^{iQ \cdot r_d} e^{-W_d}. \] (4-19)

The sum is over the \( d \) atoms in a unit cell, and \( b_d \) and \( e^{-W_d} \) are the scattering length and Debye-Waller factor for the \( d^{th} \) atom.

The relationship of the Bragg cross-section to the soft mode behavior in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \) will be considered now. In the simplest example of a second order structural phase transition, the distortion of the high temperature phase involves atomic displacements which can be described by a single normal mode; the amplitude of the distortion is then the order parameter of the transition. In \( \text{La}_2\text{CuO}_4 \) the displacements of the atoms in the distorted phase can be determined from table 2.1. A simple calculation reveals that the elastic structure factor given in equation 4-19 is proportional to the amplitude of the distortion at the orthorhombic superlattice peak positions shown in figure 4.9. Thus the Bragg cross-section, equation 4-18, measures the temperature dependence of the order parameter.

![Figure 4.9. Nuclear Reciprocal Lattice](image)
The coherent one-phonon cross-section is

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \sum_j |f_j(Q')|^2 S_{ij}(Q', \omega)$$  \hspace{1cm} (4-20)

where $S_{ij}(Q', \omega)$, the scattering function, is defined by

$$S_{ij}(Q', \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} \langle P^i(-Q', 0) P^j(Q', t) \rangle \, dt.$$  \hspace{1cm} (4-21)

Here $f_j(Q')$ is the inelastic structure factor and $P^j$ the phonon normal coordinate corresponding to the $j^{th}$ phonon branch.

The inelastic phonon structure factor in equation 4-20 is

$$f_j(Q') = \sum_d b_d m_d^{-1/2} (Q' \cdot \hat{e}_{dj}) e^{iQ' \cdot \tau_d} e^{-W_d}$$  \hspace{1cm} (4-22)

where the sum is over the $d$ atoms in a unit cell, $m_d$ is the mass of the $d^{th}$ atom, and $\hat{e}_{dj}$ is the polarization vector of the $d^{th}$ atom for the $j^{th}$ phonon branch. Measurements of the inelastic structure factor can in principle determine the atomic displacements of a phonon. For this thesis, the only important aspect of $f_j(Q')$ is that it causes the intensity of one-phonon scattering to be approximately proportional to $Q^2$.

The one-phonon scattering function, equation 4-21, is related to the imaginary part of the dynamic susceptibility of the system through the fluctuation-dissipation theorem$^1$

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\[ S(Q', \omega) = \frac{\hbar}{\pi} \left( \frac{1}{e^{\hbar \omega/k_B T} - 1} \right) \text{Im}(\chi(Q', \omega)). \] (4-23)

The important point is that a property of the system which can be easily calculated from theoretical models, \( \text{Im}(\chi(Q', \omega)) \), is directly related to the scattering cross-section. Note that this relation holds for all Van Hove scattering functions, whether they are magnetic or structural. By applying a Kramers-Kronig relation to \( \text{Im}(\chi(Q', \omega)) \), it can also be shown that the real part of the static susceptibility is proportional to the integral over energy transfer of the high temperature limit of \( S(Q', \omega) \)

\[ \int_{-\infty}^{\infty} S(Q', \omega) d\omega = k_B T \chi(Q'). \] (4-24)

A simple example will illustrate the usefulness of these relations. Consider a structural phase transition in which classical atoms distort continuously into a low temperature phase. In the harmonic approximation the Hamiltonian of the distortion mode will be

\[ H = \frac{1}{2} p^2 + \frac{1}{2} \omega_{ph}^2 q^2 - Bq. \] (4-25)

Here \( p \) is the momentum and \( q \) the displacement of the distortion, and \( B \) is a field which couples to the displacement. In a ferroelectric system, the field would just be an ordinary uniform electric field. The partition function and then the static susceptibility may be easily calculated for this transition, the result is

\[ \chi^{-1} = -\left( \frac{\partial^2 G}{\partial B^2} \right)^{-1} = \omega_{ph}^2. \] (4-26)

This relation is only exact for classical harmonic crystals, though it is applied
extensively to real systems where anharmonic effects are in fact necessary to induce
the transition. For this reason, it is more appropriate to regard $\omega_{ph}$ as a renormalized
phonon energy. To relate the susceptibility given in equation 4-26 to a scattering
cross-section, equation 4-24 may be applied to give

$$\int_{-\infty}^{\infty} S(Q',\omega)\,d\omega = \frac{k_B T}{\omega_{ph}^2}.$$  \hfill (4-27)

In order to take into account anharmonic phonon-phonon interactions, a
phenomenological damping term may be added to the Hamiltonian given in equation
4-25; the dynamic susceptibility of the oscillator then is

$$\chi^{-1}(Q',\omega) = \omega_{ph}(Q')^2 - \omega^2 - i\omega \Gamma$$  \hfill (4-28)

where $\Gamma$ is the phenomenological damping constant. Equations 4-23 and 4-28 yield a
useful form for the dynamic scattering function

$$S(Q',\omega) = \frac{1}{\pi} \left[ \frac{\omega}{1 - e^{-\omega k_B T}} \right] \left[ \frac{\Gamma}{(\omega^2 - \omega_{ph}(Q')^2 + (\Gamma \omega)^2) \right].$$  \hfill (4-29)

This is the scattering function to which the data presented in chapter 5 have been fit.
Further, it is easy to show that the integral over $d\omega$ of the high temperature limit of
equation 4-29 is consistent with equation 4-27. In summary, the one-phonon cross-
section, equation 4-20, measures the imaginary part of the dynamic susceptibility
$\chi(Q',\omega)$, and the energy of the soft phonon squared, $\omega_{ph}^2$, is the inverse of the static
susceptibility $\chi(Q')$.

4.3 Neutron Scattering Technique

In this section, a general discussion of the procedures used to measure the scattering function will be reviewed. Since all of the experiments described in this thesis were done at the High Flux Beam Reactor at Brookhaven National Laboratory, a few of the procedures described here may be site specific. More detailed information about instrumental effects and the corrections used to account for them may be found in appendix A of this thesis and the research memos of the Brookhaven National Laboratory neutron scattering group.

There are two types of 3-axis scans which can be done easily with the spectrometers at Brookhaven, constant-Q and constant-E scans. In the constant-Q scan, the momentum transfer is held fixed while the energy transfer is scanned; in a constant-E scan the energy transfer is held fixed while the momentum transfer is scanned. Note that the momentum transfer can only be scanned within the scattering plane in the constant-E scan. Figure 4.10 illustrates the two scans.

![constant-Q and constant-E scans](image)

**Figure 4.10.** Constant-E and Constant-Q Scans
The ellipse in figure 4.10 represents the resolution volume of the instrument; when this ellipse passes through the dispersion curve the scattering intensity increases. It would seem to be a simple procedure to map out the geometry and intensity distribution of $S(Q',\omega)$; however, there are two interrelated problems which have made neutron scattering experiments on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ extremely difficult:

(i) The neutron flux is low enough to require that the resolution of the spectrometer be adjusted constantly in order to even see a signal. Moreover, resolution effects can change the character of a signal extensively, so they must always be considered when interpreting data.

(ii) Once a signal has been found, a variety of tests must be made in order to determine whether it is of magnetic, structural, or nonintrinsic origin. This has been a particularly difficult problem in the studies of the magnetism in heavily doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, since even under the best conditions the intrinsic signal is so weak that it is comparable to the nonintrinsic background.

Point (i) will be addressed first. The instrumental resolution is primarily a function of $E_i$, $E_f$, $Q$, and the collimation of the instrument, which is determined by four Soller slits placed before and after the monochromator, sample, and analyzer crystals. There are consequently seven variables which can be adjusted to some extent in order to change the resolution.

A few of the limitations on the variables which determine the instrumental resolution will be described here. First, the spectrometer is always run with either $E_i$ or $E_f$ fixed at $\sim 14.7$ or $\sim 30.5\text{meV}$. As discussed in appendix A, these particular
energies are chosen in order to optimize the efficiency of pyrolytic graphite filters which eliminate most $\lambda/2$ and $\lambda/3$ higher order contamination. The resolution also depends on whether $E_i$ or $E_f$ is held fixed; however, for reasons discussed in appendix A most scans were taken in the $E_f$ fixed mode. Second, $Q$ can be changed considerably when examining two dimensional scattering by changing the position on the rod where the measurement is done. Although this procedure does change the resolution somewhat, it is usually done to produce the focusing effects described later in this section. Third, the angular divergence of the Soller slits may be chosen to be either 20°, 40°, or 80°.

The instrumental resolution appropriate for 3-axis scans can be modeled by a four dimensional ellipsoid in momentum-energy space.¹ A representation of the resolution ellipsoid within the scattering plane-energy axis subspace is shown in figure 4.10.

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Figure 4.10. Resolution Ellipsoid

The projections of the resolution ellipsoid onto the scattering plane and the energy axis provide a good measure of the resolution characteristics in a given configuration. These quantities are listed in appendix A for a variety of spectrometer configurations. Generally, the size of the resolution ellipsoid increases when $E_f$ (or $E_i$) is set at 30.5meV and when the collimation is increased. An increase in the size of the resolution ellipsoid boosts the strength of a signal; however, the background also increases so this procedure does not always increase signal visibility. The art of adjusting the spectrometer resolution so that a signal can be measured can only be learned by actually doing neutron scattering experiments; some of the configurations that were used to measure particular aspects of the scattering in $La_{2-x}Sr_xCuO_{4-y}$ are mentioned in chapters 5, 6, and 7.

So far, only the resolution within the scattering plane has been considered. The fourth dimension of the resolution ellipsoid refers to the $Q$ resolution out of the scattering plane. The collimation in the vertical or out of plane direction is fixed; consequently the resolution in this direction is determined only by $E_i$ or $E_f$. In order
to increase the overall signal, the vertical collimation has been made coarser than the in plane collimation, with the result that the $Q$ resolution itself at a given energy transfer is somewhat larger than the in plane $Q$ resolution. In general, the resolution in this direction is much larger than the width of the signal, so that an automatic integration of the scattering occurs. In the majority of the magnetic scattering experiments presented in chapters 6 and 7, the sample was oriented so that the vertical resolution ellipse spanned the "ice cream cone", as shown in figure 4.11.

![Diagram of Resolution Ellipsoid](image)

**Figure 4.11.** Orientation of Resolution Ellipsoid in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ Experiments

Because of the coarse vertical resolution, the scattering is smeared so that the scan depicted in figure 4.11 appears to be a single peak; this is to be contrasted with the two peak structure of the actual scattering. In general, instrumental resolution smears the scattering signal to some extent.

Detailed formulas of the resolution function were developed by Cooper and Nathans in the 1960's. The observed scattering intensity, including resolution effects, can be compared to theoretical cross-sections by convolving the theoretical cross-section with the instrumental resolution function.
\[ I_{\text{obs}}(Q', \omega) = \int R(\Delta', \omega') \left( \frac{d^2\sigma}{d\Omega dE_f} (Q' - \Delta', \omega - \omega') \right) d\Delta' d\omega'. \]  

(4-30)

Here \( R(\Delta', \omega') \) is the Cooper-Nathans resolution function.¹ Computer programs for calculating the 3-axis resolution function and performing the convolution have been developed at Brookhaven National Laboratory; a version of the Brookhaven programs which has been rewritten in the C language for use on MIT x-ray group computers is described in appendix A.

Modifications of the 3-axis resolution function described above to account for 2-axis resolution effects in energy integrating scans are relatively straightforward. Since all neutrons which are diffracted off the sample are detected, the resolution ellipsoid for 2-axis scans becomes elongated along the direction of \( \kappa_f^* \). The range of \( k_f \) is then 0 to \( \sim (k_i + \sqrt{k_B T/2.072}) \), which corresponds to \( \omega = E_i \) and \( \omega \sim -k_B T \) respectively. With \( \kappa_f^* \) along \( \mathbf{B}^* \), the projection of the resolution ellipsoid on the scattering plane would look like figure 4.12

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¹ Cooper, M. J., Nathans, R., Acta Cryst. 23, 357 (1967); A24, 481 (1968); A24, 619 (1968); A24, 624 (1968).
There are two important aspects of the 2-axis scattering geometry which simplify the resolution convolution. First, the cross-section is independent of the momentum along the rod. Second, under the assumptions of equations 4-11 and 4-12, the integration over energy transfer is performed automatically. This leaves only a two-dimensional convolution integration over the momentum transfers perpendicular to the Bragg rod and out of the scattering plane. The resolution out of the scattering plane is the same as in the 3-axis configuration; the resolution perpendicular to the Bragg rod can be measured directly from a (1,0,0) 3-D Bragg peak or calculated using the Cooper-Nathans formalism. A program for fitting 2-axis scans to equation 4-13 convolved with the 2-axis resolution function is described in appendix A.

The elongated nature of the 2-axis resolution function projection shown in figure 4.12 suggests that the signal and more importantly the signal to noise ratio may also be enhanced in 3-axis experiments if the long axis of the projection is oriented parallel to the 2-D rod of magnetic scattering. A focussing effect of this type has been extensively exploited in the experiments described in chapter 7; the optimum focussing...
position depends on the geometry of the scattering as well as the instrumental resolution function, however. To exploit instrumental focussing in 3-axis experiments, the k position along the 2-D magnetic rod at which one does a scan must be varied as the energy is changed. The focussing position has in practice been determined experimentally, although computer simulations which include instrumental resolution effects predict the focussing position reasonably well.

Point (ii), the determination of the origin of a signal, shall be considered now. The problem is that at a given energy and momentum transfer magnetic, structural, and nonintrinsic scattering processes can all produce a signal. Proving that a signal is intrinsic has been particularly difficult in the studies of the magnetism in heavily doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y$, since even under the best conditions the intrinsic signal is comparable to the background scattering. An example of this difficulty may be seen in figure 4.13, which shows the magnetic scattering seen in a 2-axis scan with the trajectory shown in figure 4.8.¹

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Figure 4.13. 2-axis Scan of an $x = 0.06$ Sample of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y$

The background is comparable to the signal, and some spurious scattering can be seen at low $h$ values.

To prove that a signal such as that shown in figure 4.13 is intrinsic, the Brookhaven-MIT-NTT-Tohoku collaboration has extensively applied the Shirane principle:

There are many non-intrinsic processes which can create additional scattering intensity, but there are basically no processes by which an intrinsic signal intensity can be decreased.

Although this may seem to be a trivial statement, it is only through the proper application of the Shirane principle that the experiments described in chapter 7 were successfully completed. Application of the Shirane principle in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y$ system can be reduced to four simple tests:

(a) An intrinsic signal must have the full symmetry of reciprocal lattice space, since
almost no parasitic scattering processes exhibit this symmetry. Typically, one checks
to see if identical scattering is found at $-Q^\prime$ and $+Q^\prime$.

(b) An intrinsic signal must be observable under several different experimental
conditions. For example, changing the incident neutron energy or the collimation
slightly will not change an intrinsic signal.

(c) An intrinsic signal must have reasonable energy and temperature dependences. As
stated in equations 4-9 and 4-29, the temperature dependence of the intensity of both
magnetic and lattice excitations generally (but not always) follows the bose factor. All
cross-sections must also follow the principle of detailed balance, which states that
$S(Q^\prime, -\omega) = e^{-\omega k_B T} S(Q^\prime, \omega)$. Further, one can distinguish between phonons and
magnetic excitations by noting that the phonon inelastic structure factor given in
equation 4-22 has a $Q^2$ dependence, while magnetic excitations will follow the
magnetic form factor shown in figure 4.2.

(d) An intrinsic signal must be observable in more than one sample.
4.4 Crystal Growth and Characterization

The field of high-\(T_c\) research has been dominated by experimental results, and the best experiments can only be done on single crystal samples. Consequently the vast majority of important results in this field have been obtained by research groups which have access to high quality single crystals. In this regard, the MIT neutron scattering group has been fortunate because it has been able to collaborate with four of the most successful crystal growth groups in the world, the groups at MIT, NTT, IMS, and Yamanashi University. The techniques that these groups have used to grow large single crystals, along with the extensive measurements that have been employed to characterize the samples, will be described in this section.

The basic idea behind all crystal growing techniques is to induce large crystals to solidify out of a molten solution of the desired material. There are, however, a number of problems which can inhibit the growth of large high quality crystals. The crystals might incorporate impurities, multiple small and useless crystals might grow, or the composition may not be that desired. The following discussion will outline some of the techniques that have been used to overcome these problems.

The first major obstacle in growing \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) is that the material melts at such a high temperature (1370°C) that any crucibles used to hold a molten solution will oxidize and react with it. The method used by the MIT and NTT groups to alleviate this problem is to add another material, a flux, in order to lower the melting point by several hundred degrees. The molten material can then be held in a platinum crucible. The first \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) crystals were grown by P. Picone at MIT using a lithium borate flux. Unfortunately, Li atoms were incorporated into the crystals;
nonetheless the first neutron scattering experiments were successfully carried out on these samples.\(^1\) A few months later Y. Hidaka of NTT discovered that La\(_{2-x}\)Sr\(_x\)CuO\(_4\) can grow in a CuO flux;\(^2\) this is very fortunate, because no impurity atoms from the flux are incorporated in the crystals.\(^3\) Almost all of the samples examined in this thesis were grown by the CuO flux technique.

Another problem associated the growth of La\(_{2-x}\)Sr\(_x\)CuO\(_4\) is inducing the growth of large crystals as opposed to multitudes of small crystals. Since it is necessary to have crystals of at least 0.5 cm\(^3\) volume to do inelastic neutron scattering experiments, solving this problem was crucial. The MIT crystal growth group uses a top seeded solution technique to overcome this obstacle; a seed crystal attached to a Pt wire induces the growth of only one large single crystal.\(^4\) Using this method large (up to 4 cm\(^3\)) plate-like single crystals with the orthorhombic b axis along the thin direction have been grown.

The most serious problem in the growth of single crystals of La\(_{2-x}\)Sr\(_x\)CuO\(_4\) has been incorporating large concentrations of Sr into a sample. When a crystal is grown, specific ratios of La\(_2\)O\(_3\), SrCO\(_3\) and CuO are the used as starting materials. However, the amount of Sr which is incorporated into a crystal, x, is less than the amount which was in the melt, x\(_m\); x varies from ~ 0.015 to ~ 0.15 as x\(_m\) varies from ~ 0.02 to ~ 0.5. Moreover, the oxygen content of the La\(_{2-x}\)Sr\(_x\)CuO\(_{4-y}\) crystal can change from

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3. There is still some debate about whether Pt from the crucible is incorporated into CuO flux grown crystals.
being too much \( y < 0 \) to too little \( y > 0 \), depending on the amount of Sr incorporated and the growth conditions. Generally, oxygen deficiencies become larger as the Sr concentration is increased. The fact that both Sr and O are non-stoichiometric can cause confusion in the interpretation of experimental results; extreme care must therefore be taken in characterizing the samples. However, the most discouraging aspect of this whole problem has been that no samples with superconducting transition temperatures greater than \( \sim 10^9 \text{K} \) have been grown with the CuO flux technique.

After 1½ years, a second method for growing \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), the traveling-solvent floating zone technique, was successfully applied.\(^1\) The primary advantage of this technique over the top seeded solution technique is that it produces crystals with large strontium concentrations and no apparent oxygen deficiencies. Single crystal samples with superconducting transition temperatures up to 33K and volumes up to \( \sim 0.6 \text{ cm}^3 \) have been grown. In this technique appropriate amounts of \( \text{La}_2\text{O}_3 \), \( \text{SrCO}_3 \) and CuO are first compressed under very high pressure into a rod. This rod is then heated by halogen lamps so that only a very small portion of the rod is in the liquid phase at any given time. Crystal growth is accomplished by slowing moving the heated lamps relative to the rod, leaving a single crystal behind.

Once a crystal is grown, it is important to characterize it as thoroughly as possible. Evidence indicative of the necessity for systematic sample characterization may be found in much of the early high-\( T_c \) literature; there are, unfortunately, a large

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number of experimental results which are useless because the samples studied were of low quality. Several aspects of a sample must be known in order to make useful interpretations of neutron scattering experiments:

(1) *The strontium and oxygen concentrations.*

(2) *The temperatures of any structural, magnetic and superconducting transitions.*

(3) *The magnitude of any strontium and oxygen concentration gradients.*

(4) *If a sample exhibits superconductivity, the superconducting fraction.*

In order to characterize the samples, a variety of measurements in addition to neutron scattering have been performed. These include electron probe microanalysis (EPMA), transport, magnetization, and muon spin resonance studies. A table listing the properties of all samples studied at the reactor at Brookhaven is given in appendix B, and descriptions of the measurements done on individual samples are given in chapters 5, 6, and 7. Some of the general characterization methods will be considered below.

Electron probe microanalysis (EPMA) is the standard technique for determining the composition of a sample. There are, however, at least two reasons why other methods should be used in conjunction with EPMA. First, EPMA is a surface sensitive probe, so other bulk sensitive probes should be used to confirm that the interior of a sample has the same composition as the surface. Second, the oxygen content of a sample cannot be accurately determined with EPMA. Other experiments which have been done to determine the composition of samples include measurements of the lattice constants, the structural and superconducting transition temperatures, and
the $\mu$SR spin freezing transition temperature.

Figure 4.14 shows the room temperature lattice constants of the single crystals used for neutron scattering experiments\(^1\) and oxygenated ceramics.\(^2\)

![Graph showing lattice constants](image)

**Figure 4.14.** Room Temperature Lattice Constants of $La_{2-x}Sr_xCuO_{4-y}$

In the single crystal data on the left, the orthorhombic $b$ axis is equivalent to the tetragonal $c$ axis of the ceramic data on the right. Experiments on ceramics\(^2\) indicate that the orthorhombic $b$ axis lattice constant decreases when oxygen is removed from the system. Since the lattice constants of the single crystals studied in this thesis are systematically smaller than those of fully oxygenated ceramics,\(^3\) it would appear that the single crystals are oxygen deficient. Oxygen deficiency is also reflected in the superconducting transition temperatures of the single crystals, which are systematically lower than the transition temperatures of oxygenated ceramics shown in figure 4.15.

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3. Samples grown by the traveling-floating zone method are apparently not oxygen deficient; the only sample grown by this method which is examined in this thesis is labeled KOS-1.
Figure 4.15. Superconducting Transition Temperatures in Oxygenated Ceramics

Another property by which both strontium and oxygen concentrations can be estimated is the tetragonal to orthorhombic structural phase transition temperature, $T_0$. This transition can be measured by monitoring the temperature dependence of the orthorhombic distortion, or as discussed in section 4.2, the intensity of a superlattice peak. The dependence of the transition temperature on strontium$^1$ and oxygen$^2$ content is illustrated in figure 4.16.

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Figure 4.16. Structural Transition Temperature in La$_{2-x}$Sr$_x$CuO$_{4-y}$

The data on the left show the dependence of $T_0$ on strontium content, while the data on the right illustrate the dependence of $T_0$ on oxygen content. $T_0$ is a strong function of both the oxygen and strontium concentrations; this property makes $T_0$ a particularly good indicator of composition. Unfortunately, only limited data is currently available for the dependence of $T_0$ on $y$ in strontium doped samples; Johnston$^1$ found that $T_0$ varies between $-300$K and $-20$K when $y$ varies between 0.05 and 0.00 in an $x = 0.2$ sample. Work is currently being done to map out the entire ($x$, $y$, $T_0$) phase diagram.

Muon spin resonance ($\mu$SR) has also been used to determine the composition of a limited number of samples. As mentioned in chapter 2, La$_{2-x}$Sr$_x$CuO$_{4-y}$ has a spin glass-like transition which can be determined by $\mu$SR measurements. The dependence of the spin freezing transition temperature on Sr content as determined by Weidinger $et$ $al.$$^2$ is shown in figure 4.17.

Figure 4.17. Spin Freezing Transition Temperature in La$_{2-x}$Sr$_x$CuO$_4$

Since the experiments described in chapter 7 are concerned only with magnetic properties, it is reassuring to be able to estimate the composition of a sample with a magnetic measurement.

Since the oxygen concentrations of the samples studied in this thesis have not been determined definitively, a procedure for classifying the samples which does not depend on y directly has been devised. The key assumption made is that the properties of a sample depend solely on hole content, rather than on both x and y. Clearly this assumption is not entirely correct; however, if the majority of the physics is determined by mobile holes in the CuO$_2$ sheets, then it should work reasonably well. The hole concentration, p, of a sample is then estimated from figures 4.15–4.17 by assuming that p for oxygen deficient single crystals is equal to x for fully oxygenated ceramics.

Methods for estimating strontium and oxygen concentration gradients are relatively straightforward. The primary method for determining these quantities is by measuring the degree of smearing in the structural transition temperature, T$_0$. As an
example of this procedure, consider the superlattice peak intensities for the two samples of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \) shown in figure 4.18.

![Graphs showing superlattice peak intensities for \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \) samples.]

**Figure 4.18.** Superlattice Peak Intensities in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y} \)

As can be seen in the figure, the rounding in \( T_0 \) is less than 50K in both samples. The strontium concentration gradient can then be estimated from

\[
\Delta x = \Delta T \left( \frac{\partial T_0}{\partial x} \right)^{-1}.
\]  

(4-31)

Here \( \partial T_0/\partial x \sim 2000^\circ K \) is determined from figure 4.16. Similar calculations give estimates for oxygen concentrations as well. Typically, \( \Delta x \) and \( \Delta y \) are both of order 0.01–0.02 in the samples which were studied. It is important to recognize that the sharpness of the transition is sensitive to concentration gradients on length scales that are of the order of tens of angstroms. This is because the critical behavior observed at this transition deviates strongly from mean field behavior, so that the character of the
transition depends on short range fluctuations of the order parameter. The samples studied are therefore very uniform, even on microscopic length scales. Finally, it should be mentioned that estimates of the concentration gradients determined from the amount of smearing in the superconducting transition give results consistent with estimates using the structural transition.
5. Lattice Dynamics Experiments

The lattice dynamics associated with the tetragonal to orthorhombic structural phase transition will be examined in this chapter. Section 5.1 reviews the properties of soft mode phase transitions, and the neutron scattering experiments which elucidated the soft mode behavior in La$_{2-x}$Sr$_x$CuO$_4$ are presented in 5.2. An analysis of the transition using Landau theory is given in 5.3. In section 5.4 the possible connections between structural transitions and superconductivity will be discussed.
5.1 Soft Modes and Structural Instabilities

The transition between the $I4/mmm$ tetragonal structure and the Cmca orthorhombic structure involves primarily the rotation of CuO$_6$ octahedra, as shown in the top of figure 5.1. The bottom part of figure 5.1 illustrates the long range nature of the distortion; the rotations are staggered, which causes the size of the unit cell to double at the transition. There are actually two perpendicular axes within the CuO$_2$ sheets about which the octahedra can rotate. Samples therefore break up into domains of each orientation in the orthorhombic phase, that is, they become twinned. The most important aspects of the atomic displacements are that they are small and, as demonstrated in figure 4.18, they go continuously to zero at the transition temperature, $T_0$. This suggests that this transition is driven by a soft phonon mode.
Figure 5.1. Atomic Motions at the Structural Phase Transition

The basic idea behind the soft mode description of a structural phase transition is that the displacements of atoms in the low temperature phase represent the "freezing in" of a particular normal mode of the high temperature phase. In a Landau theory of the transition, the amplitude and symmetry of the order parameter are then just those of the soft mode. Further, from equation 4-26 the energy squared of the soft mode corresponds to the inverse of the static susceptibility, which means that the energy of this mode must go to zero at the transition. Clearly the most important task in
studying such a transition is identifying the symmetry of the soft mode, since once the symmetry of the order parameter is determined the free energy for the transition may be written down and a Landau theory or renormalization group analysis performed.

The soft mode responsible for the transition in La$_{2-x}$Sr$_x$CuO$_4$ was determined by Birgeneau et al.\textsuperscript{1} soon after high-$T_c$ superconductivity was discovered. Figure 5.2 shows the phonon dispersion along the $(\zeta,\zeta,0)_T$ direction in a sample of La$_2$CuO$_4$ with $T_0 = 423K$.

![Figure 5.2. Soft Mode Energy in La$_2$CuO$_4$ and I4/mmm Brillouin Zone](image)

At the $(\frac{1}{2},\frac{1}{2},0)_T$ zone center position, the energy of the optical mode labeled $\Sigma_4$ is $\approx 3.5$meV at 573K, decreases to 0 at $T_0 = 423K$, and then climbs back up to $\approx 3.5$meV at 295K. Clearly, this is the soft phonon. In standard nomenclature, the $(\frac{1}{2},\frac{1}{2},0)_T$ position is known as the X point; a picture of the body centered tetragonal Brillouin zone which labels this position is shown on the right in figure 5.2. Note that the

tetragonal \((1/2,1/2,0)_T\) position corresponds to orthorhombic superlattice positions in figure 4.9. The symmetry of the soft mode was determined by using compatibility relations obtained from W. Weber\(^1\) and by measurements of the inelastic structure factor at various momentum transfers. Labels for the symmetry of phonons are not unique; the soft mode branch in Weber's notation is \(\Sigma_4\), while it is \(\Delta_4\) in "standard" notation. At the \(X\) point the "standard" label for this branch\(^2\) is \(B_{3g}\).

One might have thought that structural transitions in \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) were reasonably well understood after the soft mode was found experimentally. There still were a number of unresolved problems, however:

(a) As discussed in appendix C, the soft mode is doubly degenerate, which means that the order parameter for the transition has two components.\(^3\) Physically, this is the reason why twinning occurs. In the tetragonal phase, the two components correspond to degenerate phonon modes with wave vectors at \((1/2,1/2,0)_T\). In the orthorhombic phase, the degeneracy of the modes is lifted, and the two phonons should have distinct energies. This is where the unresolved question occurred; only one of the modes had been discovered in the orthorhombic phase.

(b) Structural instabilities present in the orthorhombic phase were not understood. The most direct evidence that the orthorhombic phase is unstable is found in \(\text{La}_{2-x}\text{Ba}_x\text{CuO}_4-y\); Paul \textit{et al.}\(^4\) and Axe \textit{et al.}\(^5\) showed that a structural transition out of

the orthorhombic phase can occur at certain Ba doping concentrations. Additional evidence for structural instability was found in measurements of the sound velocity;¹ as discussed in chapter 2, the acoustic modes are unusually soft in the orthorhombic phase, which suggests that the system is unstable.

(c) The connections, if any, between the superconductivity and structural transitions had not been investigated thoroughly. This was primarily because no large single crystal superconducting samples were available until the spring of 1988.

---

5.2 Experimental Results

Neutron scattering experiments\(^1\) were performed on three different single crystal samples. In order to characterize the samples, a series of measurements following the procedures outlined in chapter 4 were carried out; a summary of the physical properties of the samples is given in Table 5.1.

**TABLE 5.1. Crystal Properties**

<table>
<thead>
<tr>
<th>Label</th>
<th>(x)</th>
<th>Vol(cm(^3))</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(T_0) (K)</th>
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</thead>
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<tr>
<td>MIT-10</td>
<td>0</td>
<td>1.6</td>
<td>5.359</td>
<td>13.152</td>
<td>5.405</td>
<td>503</td>
</tr>
<tr>
<td>IMS-1</td>
<td>0.08</td>
<td>1.6</td>
<td>5.364</td>
<td>13.189</td>
<td>5.364</td>
<td>381</td>
</tr>
<tr>
<td>MIT-13</td>
<td>0.14</td>
<td>1.0</td>
<td>5.357</td>
<td>13.221</td>
<td>5.357</td>
<td>224</td>
</tr>
</tbody>
</table>

The undoped sample, MIT-10, is an insulator which undergoes a three-dimensional (3-D) antiferromagnetic transition at \(T_N = 240\)K. The \(x = 0.08\) sample undergoes a superconducting transition; the midpoint of the transition as measured by the resistivity was \(-12\)K, and the resistivity was zero at 4.2K. Susceptibility measurements on a piece from the edge of the \(x = 0.08\) sample indicate that 15% of the flux was excluded at 5K in zero field cooled experiments. Indications of a rather broad superconducting transition in the \(x = 0.14\) sample were also observed; the resistivity began to drop at \(-25\)K, but the sample still had a finite resistance at the lowest temperature measured (2.5K). In both Sr-doped samples no 3-D antiferromagnetic transition occurs.

---

Most measurements were performed in the orthorhombic (h,k,0) and (0,k,l) reciprocal lattice zones shown in figure 5.3.

![Diagram of a reciprocal lattice grid with nuclear and superlattice peaks labeled.](image)

**Figure 5.3.** Nuclear Reciprocal Lattice

Since the orthorhombic cell that is used for indexing the peaks is twice as big as the primitive Cmca cell, not every orthorhombic reciprocal lattice position is a Cmca Bragg position. One way to demonstrate this is to look up the general conditions limiting Bragg reflection for the Cmca space group in the *International Tables for X-ray Crystallography*. One finds that all Bragg positions must have $h + k = 2n$ where $n$ is an integer. Thus only $\frac{1}{2}$ of the positions with integer $h$, $k$, and $l$ are actually Bragg positions. In the experiments performed here, most of the measurements were performed around the (0,2,3) zone center superlattice peak, but because of twinning phonons around the (3,2,0) zone boundary position were simultaneously measured. Since the (0,2,3) mode has a zone center wave vector, it is the mode which condensed at the transition. That is, it corresponds to the actual distortion present in the orthorhombic phase.
Neutron scattering experiments were conducted on the triple axis spectrometers H7 and H4M at the Brookhaven High Flux Beam Reactor. The detected neutron energy was fixed at $E_r = 14.7\text{meV}$, and different combinations of 20' and 40' collimators were used depending on the conflicting requirements of intensity and resolution. Higher order neutrons were removed by a pyrolytic graphite filter mounted after the analyzer crystal.

As a preliminary experiment, the order parameter of the structural transition was measured in each of the three samples. Figure 5.4 shows the superlattice peak intensity versus temperature for the three samples, which from the discussion following equation 4.18 measures the order parameter. The solid lines represent the power law $I = I_0(T_0 - T)^2\beta$. Values of $\beta$ for the lines shown are 0.33, 0.37, and 0.34 for $x = 0$, 0.08, and 0.14, respectively. Unfortunately, the data are not sufficiently accurate to warrant interpretation of the values for $\beta$ in terms of critical exponents. Nonetheless, the data were still useful for finding concentration gradients. By using the procedures outlined in chapter 4, estimates for the concentration gradients of $\Delta x < 0.02$ and $\Delta y < 0.02$ were determined.
Figure 5.4. Superlattice Peak Intensities in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y$

The soft X-point phonons may in principle be measured in the vicinity of any superlattice peak position; the position chosen for this study because of its favorable intensity was the orthorhombic $(0,2,3)$, which corresponds to the tetragonal $(\frac{3}{2}, \frac{3}{2}, 2)_T$. Typical triple axis constant-$Q$ energy scans taken on the undoped sample are shown in figure 5.5. At 633K, the two X-point modes are degenerate, so only one phonon peak is present, with $\omega \sim 2.5\text{meV}$. The peak at $\omega = 0$ is a "central peak", a phenomenon which arises from impurities in the system.¹

---

Figure 5.5. Constant-Q Phonon Scattering Scans for La$_2$CuO$_4$

At 493K, a temperature very near the structural transition ($T_0 = 503$K), the phonons are overdamped so a single broad peak of scattering is seen. Physically, it is reasonable that the phonons are overdamped since it costs nearly zero energy to excite the modes; that is, $k_BT \gg \omega_{ph}$. In fact, most of the phonon energies were measured at the $(0,2,3.075)$ position instead of the $(0,2,3)$ position because the soft phonons at the $(0,2,3)$ position became so heavily overdamped near $T_0$ that they could not be resolved. At 379K two distinct peaks from the now nondegenerate phonon modes can be seen at $\omega \sim 3.5$meV and $\omega \sim 11$meV. The mode with the higher energy is the
(0,2,3) zone center mode, while the lower energy one is the (3,2,0) zone boundary mode. The method used to identify the modes is discussed later. Note that at 379K the peak at \( \omega = 0 \) arises primarily from the Bragg cross-section, equation 4-18.

A second example of phonon scattering is shown in figure 5.6. Here the sample is the \( x = 0.08 \) superconductor with \( T_0 = 381K \).

![Phonon Scattering Scan](image)

**Figure 5.6.** Constant-Q Phonon Scattering Scans for \( \text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4-y \)

Both of these scans were taken at temperatures well below \( T_0 \), and only the (3.05,2,0) zone boundary mode was measured. There are two important aspects to the data shown in figure 5.6. First, the energy of the zone boundary mode is unusually low, and second, it is decreasing with decreasing temperature. This behavior suggests that the orthorhombic phase is inherently unstable; a specific mechanism for structural transitions involving the (3,2,0) mode will be discussed in section 5.3.
Data analysis will be discussed now. The scans were first corrected for residual higher-order neutron contamination using the procedure discussed in appendix A. Fits were then made to the damped oscillator cross section, equation 4-29,

\[
S(Q, \omega) = \frac{I_{ph}}{\pi} \left( \frac{\omega}{1 - e^{-\omega k_B T}} \right) \left( \frac{\Gamma}{(\omega^2 - \omega_{ph}^2)^2 + \Gamma^2 \omega^2} \right) + I_G e^{-\omega^2/2\sigma^2} \tag{5-1}
\]

convolved with the instrumental resolution function. The Gaussian in equation 5-1 has been added to fit the overdamped "central peak" \( T > T_0 \) or superlattice peak \( T < T_0 \). In the fits, \( E_{ph} \) was assumed be constant within the instrumental resolution function; that is, the dispersion of the phonons was not taken into account. From these fits, the energies of the phonons, \( \omega_{ph} \), were determined.

The temperature dependence of the soft mode energies is shown in figure 5.7; the lines are guides to the eye. As discussed above, the mode is heavily overdamped at the \((0,2,3)\) and \((3,2,0)\) positions, so the energy at a position slightly off from the X-point was actually measured.

---

Figure 5.7. X-point Phonon Energies

The phonon energies decrease near $T_0$; they do not go to zero, however, because their wave vectors were not exactly at the X-point. It is nonetheless clear that the X-point mode went soft at the structural transition. Both the (0,2,3) zone center and the (3,2,0) zone boundary modes can be seen at temperatures below $T_0$ in figure 5.7. In order to identify the symmetry and wave vector of the two branches, a comparison to Raman
scattering experiments,\textsuperscript{1} which can only detect zone center modes, was made. These measurements coincide with the upper branch in figure 5.7, and also identify the symmetry of the zone center mode to be $A_g$. This symmetry was expected since from Landau theory the condensed mode must have the full symmetry of the low temperature phase. The lower branch in figure 5.7 is then the uncondensed mode which has wave vector $(3,2,0)$.

Finally, a search for differences in the soft $(3,2,0)$ phonon in the normal and the superconducting states was performed. No changes in the energy or linewidth of the phonon in the $x = 0.08$ and $x = 0.14$ samples studied here were observed. In addition, measurements on $\sim 80\%$ flux exclusion samples with $T_c = 10\,\text{K}$ and $T_c = 33\,\text{K}$ also revealed no differences in the normal and superconducting states.\textsuperscript{2}


\textsuperscript{2} Axe, J. D., Chou, H., private communication.
5.3 Landau Theory Analysis

As mentioned above, once the symmetry of the order parameter is determined, a Landau free energy may be easily written down. The procedure for doing this is outlined in appendix C of this thesis, and a similar discussion is given by Evans-Lutterodt.\(^1\) The order parameter for this transition has two components \((Q_\alpha, Q_\beta)\) corresponding to modes with wave vectors at \((\frac{1}{2},\frac{1}{2},0)_T\) and \((\frac{1}{2},-\frac{1}{2},0)_T\). The lowest order terms in the free energy are,\(^2\)

\[
G = \frac{1}{2} a(T - T_0)(Q_\alpha^2 + Q_\beta^2) + u(Q_\alpha^2 + Q_\beta^2)^2 + v(Q_\alpha^4 + Q_\beta^4) + \cdots \tag{5-2}
\]

Here \(a\), \(u\), and \(v\) are weakly temperature dependent constants. The symmetry of this free energy puts this system in the 3-D XY with cubic anisotropy universality class. Although it will not be needed here, it should be mentioned that a renormalization group analysis of this model has been done by Aharony.\(^3\) Further, the order parameter data shown in figure 5.4, while not sufficiently accurate to warrant interpretation in terms of critical exponents, are consistent with both theory\(^3\) and previous experiments.\(^4\)

From equation 4-26, the soft mode energy squared is proportional to the inverse susceptibility \((\partial^2 G/\partial Q^2)^{-1}\). Using the free energy given in equation 5-2 the following relations for the soft mode energies may be obtained

---

\[ \omega_{ph}^2 = a(T - T_0) \quad (5-3a) \]
\[ \omega_{ph}^2 = 2a(T_0 - T) \quad (5-3b) \]
\[ \omega_{ph}^2 = \frac{av}{u + v}(T_0 - T) \quad (5-3c) \]

Equation 5-3a applies above \( T_0 \), while 5-3b and 5-3c correspond to the condensed and uncondensed modes respectively below \( T_0 \). In these equations, it has been assumed that \( Q_\beta = 0 \) in the Cmca phase; further, \( v < 0 \) and \( u + v > 0 \) must hold in order for equation 5-3c to be consistent. Note that the temperature slope of the energy squared of the condensed Cmca mode is indeed roughly twice the slope of the tetragonal phase phonon energy squared, which agrees with equations 5-3a and 5-3b.

The low temperature behavior of the uncondensed (3,2,0) zone boundary mode fits nicely into the Landau theory analysis. The most important features of this mode are its relatively low energy and the softening at low temperatures. The low energy of this mode suggests that the orthorhombic phase of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4-y \) is inherently unstable. Minimization of equation 5-2 reveals that only two stable phases can exist.\(^1\)


(1) A phase where one of the \( Q_i \) is zero and the other nonzero. This corresponds to the Cmca orthorhombic phase and will occur when \( v < 0 \) and \( v + u > 0 \).

(2) A phase where \( |Q_\alpha| = |Q_\beta| \). This corresponds to a tetragonal phase and will occur when \( v > 0 \) and \( 2u + v > 0 \).
Since $v < 0$ in the Cmca phase, while $v > 0$ in a low temperature tetragonal phase, any transformation between these two phases occurs when the Landau parameter $v$ approaches 0. The temperature dependence of $v$ in the orthorhombic phase may be calculated in Landau theory to be

$$v = -\frac{\omega_{ph}^2}{4Q_\alpha^2}. \quad (5-4)$$

Here $\omega_{ph}$ refers to the uncondensed (3,2,0) zone boundary phonon energy of the Cmca phase and $Q_\alpha$ is the amplitude of the order parameter. Using the $\omega_{ph}$ data in figure 5.7 and the data for $Q_\alpha$ found in Vaknin et al., the temperature dependence of $v$ may be calculated. Figure 5.8 shows the result of this calculation.

![Graph showing the temperature dependence of $v$ in La$_2$CuO$_4$.](image)

**Figure 5.8.** Temperature Dependence of the Landau Parameter $v$ in La$_2$CuO$_4$

The softening of $v$ as the temperature is lowered indicates that La$_2$CuO$_4$ has an incipient structural transition similar to those actually present in La$_{2-x}$Ba$_x$CuO$_{4-y}$.

Thus the dynamical cause of the low temperature structural anomalies in both materials has been clearly demonstrated here. Additional development of the Landau theory of low temperature structural phase transitions in La$_{2-x}$Sr$_x$CuO$_4$ may be found in Axe et al.\textsuperscript{1}

An analysis of the coupling of the orthorhombic strain to the order parameter is also interesting. As discussed in appendix C, the free energy including relevant strain terms is

\[ G = \frac{1}{2}a(T - T_0)(Q^2_\alpha + Q^2_\beta) + u(Q^2_\alpha + Q^2_\beta)^2 + v(Q^4_\alpha + Q^4_\beta) + \cdots \]
\[ + \frac{1}{2}c\eta^2 + d(Q^2_\alpha - Q^2_\beta)\eta + \cdots \]  

(5-5)

Here $\eta$ is the orthorhombic strain, $c$ the elastic constant corresponding to the orthorhombic distortion, and $d$ a weakly temperature dependent Landau parameter. Minimization of this free energy with respect to $\eta$ yields

\[ \eta = -\frac{d}{c}(Q^2_\alpha - Q^2_\beta) \]  

(5-6)

so that the renormalized free energy is

\[ G = \frac{1}{2}a(T - T_0)(Q^2_\alpha + Q^2_\beta) + \left(u + \frac{d^2}{2c}\right)(Q^2_\alpha + Q^2_\beta)^2 + \left(v - \frac{d^2}{c}\right)(Q^4_\alpha + Q^4_\beta). \]  

(5-7)

Since $Q_\beta = 0$ in the Cmca phase, the orthorhombic strain is proportional to the order parameter squared, and the overall symmetry of the free energy is unchanged. This proportionality between the strain and the square of the order parameter has in fact

been observed experimentally.\textsuperscript{1} Figure 5.9 shows the temperature dependence of both quantities in a sample of La_2CuO_4.

![Graph showing temperature dependence of strain and superlattice peak intensity in La_2CuO_4.]

**Figure 5.9.** Superlattice Peak Intensity and Orthorhombic Strain in La_2CuO_4

Although the agreement between Landau theory and experiment appears to be good here, a few words of caution are necessary. First, the experiments of Vaknin et al.\textsuperscript{2} did not indicate that the strain and the superlattice peak intensity had the same temperature dependence. Second, the atomic motions which produce orthorhombic strain do not break as many symmetries of the tetragonal phase as the B_{3g} normal mode displacements. Thus the strain need not approach zero as T \rightarrow T_0 with the same exponent as the order parameter of the transition. For this reason the strain is sometimes called a secondary order parameter of the transition.\textsuperscript{3}

\begin{itemize}
\end{itemize}
Finally, it should be mentioned that coupling between the soft (3,2,0) zone boundary mode and acoustic modes probably causes the sound velocity to remain soft in the Cmca phase, as shown in figure 2.4.\textsuperscript{1} However, no theory for this phenomenon has been developed, yet.

5.4 Structural Instabilities and Superconductivity

Because no changes in phonon linewidths or energies were observed at the superconducting transition, the low temperature structural instability of the Cmca phase manifested by the the soft zone boundary mode is almost certainly not a primary mechanism for the high temperature superconductivity. Nonetheless, structural effects may still play a secondary role in the superconductivity. Two experimental observations reinforce this line of thought:

(1) The isotope effect in La$_{2-x}$Sr$_x$CuO$_{4-y}$ is not negligible.\(^1\)

(2) A correlation between measured values of T\(_c\) and low temperature structural phase transitions in the La$_{2-x}$Ba$_x$CuO$_{4-y}$ system has been discovered by Moodenbaugh \textit{et al.}\(^2\) and Axe \textit{et al.}\(^3\)

Clearly the relationship of structural instabilities to the superconductivity is not completely understood yet. One possible explanation of point (2) above has recently been proposed by Thio \textit{et al.}\(^4\) Due to the rotation of the CuO\(_6\) octahedra, an antisymmetric exchange term is allowed in the spin Hamiltonian in the orthorhombic phase. In a low temperature tetragonal phase the antisymmetric exchange would change in a fundamental way. Experimental evidence that magnetic phenomena associated with the antisymmetric exchange can alter the conductivity has also been


\(^{4}\) Thio, Tineke, \textit{et al.}, submitted to Phys. Rev. B.
observed. Thus a low temperature structural phase transition might affect the superconductivity through magnetic effects.
6. 2-D Spin Correlations in La$_2$CuO$_4$

The spin correlations of the two-dimensional magnetism found in La$_2$CuO$_4$ will be examined in this chapter. An introduction to the issues associated with the magnetism in the undoped system is given in section 6.1. The experiments which elucidated the basic features of the system are discussed in 6.2. In section 6.3 the experimental and theoretical work which has basically resolved all aspects of the spin dynamics in La$_2$CuO$_4$ is presented.
6.1 Introduction

As discussed in chapter 2, stoichiometric La$_2$CuO$_4$ undergoes a transition$^1$ into a three-dimensional Neel state. A number of experiments have demonstrated that an appropriate model for describing the magnetism in La$_2$CuO$_4$ is the $S = 1/2$ Heisenberg model

$$H_{\text{spin}} = J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j.$$ (6-1)

This description of the magnetism arises from a localized Mott-Hubbard theory of the electronic structure. Properties of the magnetism determined through experiments done on the 3-D Neel state include:

(1) The 3-D ordered moment$^1$ is $0.5 \pm 0.15 \mu_B$, which basically agrees with theoretical predictions starting from equation 6-1 which include zero point quantum fluctuation effects.$^2$

(2) The $Q$ dependence of the experimentally determined magnetic form factor$^3$ agrees well with the calculated free ion Cu$^{2+}$ 3d$^9$ form factor.

(3) The exchange is nearly two dimensional,$^4$ since the interactions between CuO$_2$ layers are $\sim 10^{-5}$ times smaller than within the layers. The 3-D ordering is in fact a

parasitic effect which occurs only after 2-D correlations within the CuO$_2$ planes have become long ranged.

(4) The exchange is nearly isotropic within the CuO$_2$ layers. The spins do order along the orthorhombic c axis, but the gaps for producing excitations out of the plane and within the plane are only $-2.5$ and $-1.0$ meV respectively.\textsuperscript{1} These energies are very small compared to the exchange ($-135$ meV) and typical Neel ordering temperatures ($-25$ meV).

(5) The nearest neighbor exchange is much larger than the next nearest neighbor exchange \textit{etc}. Although this aspect of the exchange interactions has not been quantified, all experiments performed to date can be satisfactorily explained with the assumption of only a nearest neighbor exchange.

(6) Ordinary spin wave theory adequately describes the spin excitations in the Neel state.\textsuperscript{2}

The experiments on the 3-D Neel state demonstrate that La$_2$CuO$_4$ is an almost perfect embodiment of a 2-D S = $\frac{1}{2}$ Heisenberg model.

The experimental results cited above also show that the 3-D Neel state is very well understood and, in the end, somewhat ordinary. On the other hand, the 2-D spin correlations which exist above the Neel state are much more interesting. The 2-D S = $\frac{1}{2}$ Heisenberg model is a rather old problem whose solution had long eluded


\textsuperscript{2} Yamada, K., \textit{et al.}, accepted by Phys. Rev. B.
physicists. Moreover, since \( \text{La}_2\text{CuO}_4 \) is the first 2-D \( S = \frac{1}{2} \) Heisenberg system to be found in nature, any experimental information which can be obtained about the 2-D magnetism in this material is almost certainly going to be crucial for solving this problem.

A description of some of the theoretical work done on the 2-D \( S = \frac{1}{2} \) Heisenberg model illustrates how little was known independent of experiment. Since this model does not order at finite temperatures,\(^1\) the nature of the \( T = 0 \) ground state has been one of the most important issues to be addressed. Anderson\(^2\) argued in the 1950's that even though the staggered magnetization may be reduced, the Neel state is stable against quantum fluctuations at \( T = 0 \). This result had subsequently been proven\(^3\) rigorously for \( S \geq 1 \), but not for \( S = \frac{1}{2} \), the spin of the moments in \( \text{La}_2\text{CuO}_4 \). Qualitatively, it is tempting to believe that the extreme quantum nature of \( S = \frac{1}{2} \) moments induce large enough quantum fluctuations to disorder the system even at \( T = 0 \). Anderson himself recently suggested\(^4\) that the ground state of the 2-D \( S = \frac{1}{2} \) Heisenberg model is an RVB state, his term for a quantum disordered singlet state. However, contrary to Anderson's current point of view, a number of recent numerical calculations\(^5\) suggest that the ground state at \( T = 0 \) for the \( S = \frac{1}{2} \) Heisenberg model is still Neel ordered.

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Given all this theoretical confusion, it should be clear that the only way to definitively determine the properties of the 2-D magnetism in La$_2$CuO$_4$ is through experiment. In this regard, the fact that all experiments must be done at finite temperatures is somewhat discouraging. Nonetheless, one should be able to obtain all necessary information from the finite temperature behavior. For example, if the system orders in a Neel state at $T = 0$, then antiferromagnetic correlations with certain predictable properties should exist at finite temperatures. On the other hand, if the system has a $T = 0$ quantum disordered state, then the finite temperature spin correlations (if they exist) should reflect the inherently disordered nature of the system. The experiments described in this chapter$^1$ provided the first real information about this spin state. In addition, they inspired theory$^2$ which not only describes the magnetism of undoped La$_2$CuO$_4$ correctly, but may also prove to very important in understanding the magnetism found in doped La$_{2-x}$Sr$_x$CuO$_4$ as well.

6.2 Statics and Dynamics Experiments

Neutron scattering experiments on four different crystals of La$_2$CuO$_{4+y}$ are described in this chapter; a summary of the characteristics of these samples is given in Table 6.1.

<table>
<thead>
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<th>Label</th>
<th>$y$</th>
<th>Vol(cm$^3$)</th>
<th>$T_0$(K)</th>
<th>$T_N$(K)</th>
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<td>1.6</td>
<td>503</td>
<td>240</td>
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<td>515</td>
<td>245</td>
</tr>
<tr>
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<td>0.008</td>
<td>−2</td>
<td>515</td>
<td>245</td>
</tr>
</tbody>
</table>

The Néel temperature $T_N$ and the tetragonal-orthorhombic structural transition temperature $T_0$ were determined from the temperature dependences of the magnetic (1,0,0) and nuclear (0,2,1) superlattice intensities. All of the samples have excess oxygen; nonetheless they were all insulators. The oxygen content $y$ was determined from $T_N$ by using figure 4 in Chen et al.$^1$ and assuming that there are 0.5 excess holes produced for each oxygen added. Except where noted, all of the crystals exhibited virtually identical properties in their two-dimensional magnetism.

Experiments were carried out on the triple axis spectrometers H4M, H7, H8, and H9 at the Brookhaven High Flux Beam Reactor. Pyrolytic graphite (0,0,2) or Cu$_2$MnAl (1,1,1) crystals were used as both monochromator and analyzer for

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unpolarized and polarized neutron experiments respectively. For 3-axis scans, the spectrometers were run exclusively in the $E_f$ fixed mode. Various incident neutron energies and horizontal collimations were used in order to optimize different kinds of measurements, and pyrolytic graphite filters were used to eliminate higher order contamination.

The crystals were usually mounted with the $a^*$ (and because of twinning $c^*$) axis perpendicular to the scattering plane. In this configuration, the 2-D magnetic rods are within the scattering plane. The magnetic and nuclear reciprocal lattices for this zone are shown in figure 6.1.

![Diagram of Magnetic and Nuclear Reciprocal Lattice]

Figure 6.1. Magnetic and Nuclear Reciprocal Lattice

Because of twinning, both the $(1,k,0)$ and the $(0,k,1)$ magnetic rods are measured simultaneously. In most of the data presented below, the distortion is small enough that it may be ignored in qualitative interpretations of the data. Further, since the system has Heisenberg symmetry, both 2-D rods of scattering will have equal intensity aside from small geometric corrections.
The temperature dependence of the integrated intensity for both the 3-D (1,0,0) magnetic Bragg peak and the 2-D (1,0.59,0) magnetic rod in NTT-2 is shown in figure 6.2.

![Graph showing temperature dependence of integrated intensity for magnetic Bragg peaks.](image)

**Figure 6.2.** 3-D and 2-D Magnetic Scattering Intensity

The 3-D transition occurs at 195K, and as the 3-D intensity increases, the 2-D intensity gradually decreases. Heuristically, the 2-D scattering is being converted into 3-D scattering as the temperature is lowered. The order parameter curve for the Neel transition is characteristically 3-D in shape. This contrasts with the behavior found in K$_2$NiF$_4$, which shows clear 2-D Ising critical behavior.\(^1\) Further, the 2-D rod intensity in K$_2$NiF$_4$ is basically completely converted into 3-D peak intensity within 2% of $T_N$.

The difference between the two systems lies in the fact that a 2-D Heisenberg system can have a transition only at $T = 0$, while a 2-D Ising system will have a transition at finite temperatures. Thus the order parameter and critical scattering of previously

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studied Ising systems reflected intrinsic 2-D ordering, while the 3-D transition in La$_2$CuO$_4$ is a parasitic effect driven by weak interplanar magnetic coupling.

Three axis constant-E scans probing the magnetic excitations in NTT-2 at 300K are shown in figure 6.3. The scans follow a trajectory in momentum transfer perpendicular to the Bragg rod, so that only 2-D excitations are measured.

![Graph](image)

**Figure 6.3.** 3-axis Scans at T = 300K

The illustration on the right shows the "ice cream cone" geometry in energy-momentum space expected for ordinary magnons; clearly the geometry of the observed scattering is qualitatively similar, although the slope of the excitations is too steep to resolve the scattering into two peaks. As shown later, the 2-D magnetic correlation length at 300K is ~200Å; the system is already fairly well ordered at this temperature.
It should therefore not be too surprising that excitations qualitatively similar to ordinary antiferromagnetic magnons exist at this temperature. A lower limit for the slope of the excitations was found from the data shown in figure 6.3 to be $v > 400\text{meVÅ}$. Subsequent neutron scattering experiments done at higher resolution improved this lower limit to $v > 600\text{meVÅ}$, and light scattering\textsuperscript{1} experiments set the value at $\sim 800\text{meVÅ}$. Using spin wave theory, the exchange constant then is $\sim 135\text{meV}$, which is an unusually large value for an antiferromagnetic insulator. In fact, this anomalously large magnetic energy has encouraged many physicists to consider models of the superconductivity involving magnetism; unusually large magnetic energies might lead to unusually large $T_c$'s.

The energy dependence of the integrated 2-D scattering intensity found in NTT-7 and NTT-8 is shown in the top part of figure 6.4. Three temperatures above the 3-D Neel transition have been studied.

Figure 6.4. 2-D Integrated Intensity in La$_2$CuO$_4$

The intense scattering near $\omega = 0$ observed at 290K and 350K is believed to be similar to the central peak mentioned in chapter 5. This scattering would then be related to impurities and is not intrinsic to a 2-D $S = \frac{1}{2}$ Heisenberg system. The most interesting aspect of the scattering is the very large inelasticity; the intensity at 12meV is comparable to the intensity at lower energies. The inelasticity can be partly
explained by the large exchange; however, as discussed in chapter 4 large inelasticity is also a signature of a highly fluctuating spin system. Another explanation for this behavior then is that the extreme quantum $S = \frac{1}{2}$ nature of the spins causes them to fluctuate anomalously. Anderson therefore suggested that this unusual inelastic scattering was a signature of his RVB state.\textsuperscript{1} There are many highly fluctuating spin states which could produce this scattering, though; quantitative comparisons between experiment and theory were clearly necessary.

Measurements of the instantaneous 2-D antiferromagnetic correlation provided the first quantitative comparisons between experiment and theory. As shown in equations 4-11 and 4-12, integrating over energy transfer with a 2-axis scan will measure an equal time 2-D correlation function if most of the scattering intensity is in the interval $-k_B T < \omega < E_i$. Representative 2-axis scans of the scattering in NTT-2 are shown in figure 6.5.

Figure 6.5. 2-Axis Scans

At 523K, the scattering is relatively broad, which indicates that the spins are antiferromagnetically correlated only over very small distances. As the temperature is lowered, the width of the scattering narrows, indicating that the spins have become correlated over larger distances. The collimation for this experiment was 40'-10'-10' and the incident neutron energy was 30.5meV. Nearly identical results were obtained when the incident neutron energy was 14.7meV; this proves that most of the scattering intensity was within the interval $-k_B T < \omega < 30.5\text{meV}$, so that an instantaneous correlation function was actually measured.

To obtain quantitative information about the 2-D antiferromagnetic correlation length, the 2-axis scans were fit to two isotropic Lorentzians. The Lorentzian
lineshape was justified in equation 4-13; the scattering must be fit to two peaks in order to take into account the orthorhombic distortion. The temperature dependence of the inverse correlation length obtained from the fits is shown in figure 6.6.

![Graph showing temperature dependence of ξ⁻¹ in La₂CuO₄](image)

**Figure 6.6.** Temperature Dependence of ξ⁻¹ in La₂CuO₄

At 500K, ξ is ~40Å, while at 300K the correlation length has increased to ~200Å. Insight into the nature of this system may be obtained by comparing the experimental correlation length to the value expected for a 2-D classical Heisenberg system with exchange constant J = 135 meV. The classical expression for the correlation length is

\[
ξ = a \exp(2πJS²/k_BT)
\]

where the lattice constant \( a = 3.8 \)Å. Using this expression, at \( T = 300K \) the classical

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correlation length would be $\sim 20000\AA$. This result clearly does not agree with experiment. Qualitatively, fluctuations associated with the quantum $S = \frac{1}{2}$ nature of the system have caused the spin correlation length to be reduced by a factor of 100. Chakravarty, Halperin, and Nelson recently\(^1\) have derived an expression for the 2-D correlation length which includes quantum corrections; in their theory equation 6-2 is replaced by

$$\xi = \frac{0.5a}{1 + (k_B T/2\pi JS^2 Z/k_B T)} \exp(2\pi JS^2 Z/k_B T) \quad (6-3)$$

$$Z = \left[1 - (0.552/2S)\right] \left[1 + (0.158/2S)\right]^2$$

where the quantum renormalization factor, $Z$, is $\sim 0.6$ for $S = \frac{1}{2}$. The line in figure 6.6 shows the results of this theory. For a calculation which includes no adjustable parameters, the agreement between theory and experiment is very impressive.

Consistency checks which prove that the observed scattering is magnetic will described below. First, the polarized neutron scattering technique is used to definitively show that the signal found in La$_2$CuO$_4$ is magnetic. Second, the characteristics of the scattering which arise from the two-dimensional nature of the spin correlations are documented.

Polarized neutron scattering measurements were carried out on spectrometer H8. The instrument was run with $E_f = 41$ meV and $\omega = 3$ meV, and the collimation was 40'-80'-80'-130'. This configuration has an energy resolution of 7 meV full width at

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half maximum; the extremely coarse collimation is necessary because of the inefficiency of the polarizing Heusler crystals. The spectrometer can be run in two different modes; scattering processes where the spin of the neutron is either flipped (SF) or unchanged (NSF) are detected in these two configurations. Further, the polarization of the neutron may be chosen to be either parallel or perpendicular to \( Q' \). In order to polarize the neutron, an external magnetic field which is either along \( Q' \) (HF) or in the vertical direction (VF) perpendicular to \( Q' \) is generated.

The important aspect of polarized neutron scattering experiments which makes them so useful is that they can unambiguously determine whether a signal is magnetic. It turns out for magnetic scattering that

\[
I(\text{NSF};\text{VF}) - I(\text{NSF};\text{HF}) = I(\text{SF};\text{VF}) - I(\text{SF};\text{VF}) = S^V(Q',\omega). \tag{6-4}
\]

Here \( S^V(Q',\omega) \) is the component of the scattering function perpendicular to the scattering plane. For the magnetic signal in \( \text{La}_2\text{CuO}_4 \), twinning causes the scattering from spin correlations along both the \( \vec{a} \) and \( \vec{c} \) axes to be detected:

\[
S^V(Q',\omega) = \frac{1}{2}S^{aa} + \frac{1}{2}S^{cc}. \]

The scattering observed in NTT-2 at 200K is shown in figure 6.7.
Figure 6.7. Polarized Neutron Scattering Scans in NTT-2

It is clear that within experimental errors the NSF and SF intensity differences are the same. This confirms definitively that the 2-D scattering is magnetic.

The characteristics of the scattering arising from the 2-D nature of the spin correlations are documented here. Since no low energy two-dimensional phonon modes have been found in La$_{2-x}$Sr$_x$CuO$_4$, any scattering which is two-dimensional in character is most likely magnetic in origin. This behavior will be particularly useful in demonstrating that the scattering found in heavily doped La$_{2-x}$Sr$_x$CuO$_4$ is magnetic, since in doped samples the signal is far too weak to perform polarized neutron experiments. To prove that the scattering found above the Neel transition is indeed two dimensional, scans parallel to the magnetic rods were performed. Data taken on NTT-2 with $\omega = 6\text{meV}$ and $Q' = (1,\xi,0)$, $(0.9,\xi,0)$ are shown in the bottom of figure 6.8.
Figure 6.8. Scans Along the Rod in NTT-2

Significant scattering occurs at \((1, \zeta, 0)\) whereas at \((0.9, \zeta, 0)\) the intensity is at the background level. The scattering thus forms a rod along the orthorhombic k direction, which is the signature of 2-D correlations.

A more interesting and in some ways useful scan is shown in the top of figure 6.8. This is an energy integrating 2-axis scan. The peak at \(k = 0.57\) r.l.u. occurs because, as discussed in chapter 4, this is the position where \(K_f^2\) is parallel to the rod of scattering. There are two conditions which the scattering must satisfy in order to produce such a pronounced peak: (i) it must be two-dimensional (ii) it must be highly inelastic. These conditions are actually rather stringent; only the 2-D scattering arising from the spin correlations satisfy both of them.
6.3 Dynamics Experiments and the CHN Theory

Section 6.2 presented experimental information on the 2-D spin excitations in \( \text{La}_2\text{CuO}_4 \) available by the spring of 1988. The experimental discovery of an unusual, highly fluctuating though strongly correlated 2-D spin state stimulated a number of theoretical efforts. Among these were the work of Affleck\(^1\) and Anderson,\(^2\) who suggested that the geometry of \( S(Q',\omega) \) for the 2-D spin fluctuations would not have the simple cone shape shown in figure 4.6. Predictions that scattering would appear at positions other than at antiferromagnetic rod positions were also made. These ideas were experimentally tested\(^3\) and found to be entirely incorrect. The 2-D scattering found above the parasitic 3-D Neel transition is qualitatively similar in many respects to the scattering expected from classical 2-D antiferromagnetic spin waves.

A theory of the 2-D \( S = \frac{1}{2} \) Heisenberg model which predicted that the spin system will behave in a renormalized classical fashion has been formulated by S. Chakravarty, B. I. Halperin, and D. R. Nelson (CHN). The statics part of this theory,\(^4\) equation 6-3, was already compared to experiment in figure 6.6. CHN subsequently derived expressions for the dynamic scattering function.\(^5\) Simultaneously, K. Yamada\(^6\) and coworkers executed detailed experiments on the dynamics of the 2-D spin fluctuations in \( \text{La}_2\text{CuO}_4 \). Experiment and theory converged after these efforts.

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1. Affleck, I., private communication.
In figure 6.9 representative scans across the 2-D rod taken on NTT-7 are shown. The scattering at 3 different energy transfers (3meV, 6meV, 12meV) for 3 different temperatures (290K, 413K, 518K) is presented.

Figure 6.9. Temperature Evolution of the Dynamic Spin Correlations Above T_N

The lines in figure 6.9 represent the scattering function predicted by the Chakravarty-Halperin-Nelson (CHN) theory convolved with the instrumental resolution function. The agreement is impressive, but even more so once one recognizes that aside from an overall intensity factor, there are no adjustable parameters in the CHN theory. Only the experimentally determined spin wave velocity (~800meVÅ) and correlation length (figure 6.6) were used as input parameters in the calculation, everything else was completely determined. It is especially notable that the CHN theory was formulated
independently of experiments; in fact, the CHN theory is the only theory which has made successful quantitative predictions about the properties of La$_2$CuO$_4$ and La$_{2-x}$Sr$_x$CuO$_4$ to date.

Since the CHN theory describes the 2-D spin excitations in La$_2$CuO$_4$ so well, it is worthwhile to describe some of the essential features of the theory. The starting point of the CHN theory is the observation by Haldane$^1$ that the $S \to \infty$ limit of of the quantum 2-D Heisenberg model can be mapped on to a quantum generalization of the nonlinear sigma model (QNL$\sigma$M),$^2$ a field theory model which describes the interactions of vectors with a fixed magnitude. CHN asserted that the $S = \frac{1}{2}$ 2-D Heisenberg model can also be described by a QNL$\sigma$M; to justify this assumption they analyzed the long-wavelength, low-energy, low-temperature behavior of the QNL$\sigma$M and found it to be identical to all previously known results for the 2-D Heisenberg model. In the course of this analysis, they found that under certain conditions the QNL$\sigma$M can be mapped on to a classical rotator model. Using classical renormalization group and dynamic scaling methods, they were then able to obtain expressions for $\xi(T)$ and $S(Q,\omega)$.

The classical nonlinear $\sigma$ model and its mapping on to the classical 2-D Heisenberg model will be briefly reviewed here. The general idea behind this mapping is to find a way to do the algebra necessary for a low temperature expansion of the Heisenberg model about a fully ordered $T = 0$ state. Further, there was evidence$^2$

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$^2$ For a discussion of the classical nonlinear $\sigma$ model, see Field Theory, the Renormalization Group, and Critical Phenomena, 2nd ed. (World Scientific, Singapore, 1984), by D. J. Amit, pp. 364-381.
which indicated that long range order is primarily destroyed by fluctuations in the phase of the order parameter, rather than in its amplitude. In mapping a classical Heisenberg model on to a classical nonlinear $\sigma$ model, the components of the spins are represented by two fields, $\pi^\alpha(\mathbf{r})$ and $\sigma(\mathbf{r}) = \sqrt{1 - \pi^2(\mathbf{r})}$. The $\pi$ field corresponds to the components of the spins which do not order; for the Heisenberg model there are two such components, $\alpha = 1, 2$. The $\sigma$ field represents the longitudinal component of the spins. An expression for the partition function then is

$$Z = \int \prod_{i=1}^{N} \delta(\Omega_i^2 - 1) d\Omega_i e^{-S_{\text{eff}}}$$  \hspace{1cm} (6-5)

where the product is over the $N$ sites in the lattice and $\Omega_i$ is the spin at site $i$. The delta function insures that the spins have a fixed magnitude, $|\Omega_i| = 1$; consequently $\Omega_i$ is usually written as a unit vector $\hat{\Omega}_i$. The classical action, $S_{\text{eff}}$, is

$$S_{\text{eff}} = J \int d\mathbf{r} |
abla \hat{\Omega}|^2 + \ldots$$  \hspace{1cm} (6-6)

In terms of the $\sigma$ field, the action may be written as

$$S_{\text{eff}} = -\frac{1}{2} \int d\mathbf{r} \left[ |\nabla \sigma|^2 + |\nabla \sqrt{1 - \sigma^2}|^2 \right].$$  \hspace{1cm} (6-7)

Only terms arising from fluctuations of the phase of the ordering field appear in this expression. It should be clear from equation 6-7 how the nonlinear $\sigma$ model got its name. The problem is now in a form which can be solved to find the critical behavior etc.

Haldane's generalization of the classical nonlinear $\sigma$ model to quantum systems replaces equation 6-6 by
\[ S_{\text{eff}} = \frac{\rho_0}{2} \int_{0}^{\beta h} d\tau \int d^2 \hat{r} \left[ |\nabla \hat{\Omega}|^2 + \frac{1}{c_0^2} |\frac{\partial \hat{\Omega}}{\partial \tau}|^2 \right]. \quad (6-8) \]

Here \( \tau \) is a time-like variable and \( \rho_0, c_0 \) are bare (microscopic) values for the spin stiffness and velocity respectively. In the limit \( S \rightarrow \infty \), Haldane was able to relate these variables to parameters in the 2-D Heisenberg model. Since CHN only assume that the QNL\( \sigma \)M captures the essential physics of the 2-D \( S = \frac{1}{2} \) Heisenberg model, they regarded \( \rho_0 \) and \( c_0 \) as phenomenological parameters. By changing variables such that \( \tilde{\mathbf{y}} = \Lambda \mathbf{r} \) and \( \mu = \Lambda c_0 \tau \), a more useful form of equation 6-8 may be obtained

\[ S_{\text{eff}} = \frac{1}{2g_0} \int_{0}^{\beta h} d\mu \int d\tilde{\mathbf{y}} \left[ |\nabla \tilde{\Omega}|^2 + |\frac{\partial \tilde{\Omega}}{\partial \mu}|^2 \right]. \quad (6-9) \]

Here the coupling constant, \( g_0 \), is \( \hbar c_0 \Lambda^{d-1}/\rho_0 \). The second term in equation 6-9 takes into account quantum fluctuations of the system. It is easy to show that this term drops out in the classical limit (\( \beta \hbar \Lambda c_0 \ll 1 \)), so that equation 6-9 reduces to a form analogous to equation 6-6. It is also clear from equation 6-9 that the \( d \) dimensional quantum nonlinear \( \sigma \) model is analogous to a \( (d + 1) \) dimensional classical nonlinear \( \sigma \) model with one dimension that has a temperature dependent thickness, \( t = \beta \hbar c_0 \Lambda \).

To continue the analysis of the QNL\( \sigma \)M, CHN next lattice regularized the action in equation 6-8. That is, the system was divided up into regions of size \( b^d \), where \( b \) is a parameter which is not necessarily a microscopic lattice constant. This procedure yielded the following expression for the action

\[ S_{\text{eff}} = \frac{b^d \rho_0}{2} \int_0^{\beta_h} d\tau \left( \sum_i \frac{\partial \hat{\Omega}_i}{\partial \tau} \right)^2 + \sum_{<i,j>} \frac{|\Omega_i - \Omega_j|^2}{b^2} \right) \]  

(6-10)

Here the sum over \(<i,j>\) is restricted to nearest neighbor bonds. Further, the Hamiltonian which corresponds to equation 6-10 is

\[ H = \frac{b^d}{2} \left( \sum_i \frac{|\hat{M}_i|^2}{b^{2d} \chi_p} + \rho_0 \sum_{<i,j>} \frac{|\hat{\Omega}_i - \hat{\Omega}_j|^2}{b^2} \right) \]  

(6-11)

where \(\chi_p\), the perpendicular susceptibility, is given by \(\chi_p = \rho_0/c_0^2\). In this Hamiltonian, if \(\hat{\Omega}_i\) is interpreted as the orientation of a rodlike rotator on lattice site \(i\), then \(\hat{M}_i b^d\) is the angular momentum on that site. Thus equations 6-10 and 6-11 describe coupled rotators whose thickness in one direction is inversely proportional to the temperature. A hydrodynamic analysis of equations 6-10 and 6-11 was performed in order to compare the behavior of the QNL\(\sigma\)M to all previous results for the hydrodynamic behavior of Heisenberg antiferromagnets. With the exception of the special case of half integer spins in one dimension, no differences in the long wavelength behavior of Heisenberg antiferromagnets and the QNL\(\sigma\)M were found. This justified the assertion that the QNL\(\sigma\)M captures the essential physics of the 2-D \(S = \frac{1}{2}\) Heisenberg model.

The phase diagram predicted by equations 6-10 and 6-11 is quite interesting. First, consider the \(T = 0\) behavior. Clearly the main issue here is whether quantum zero-point fluctuations destroy long range order. The size of these fluctuations may be estimated from a harmonic-oscillator expansion; CHN found that if the coupling constant \(g_0\) were larger than a certain critical value, \(g_c\), then quantum fluctuations would destroy long range order, even at \(T = 0\). A more substantial renormalization
group analysis yielded the phase diagram shown in figure 6.10.

![Phase Diagram](image)

**Figure 6.10. Phase Diagram for the QNLσM at d=2**

In the quantum disordered region where \( g > g_c \), the magnetic correlation length remains finite at \( T = 0 \), and the ground state has a gap in its spin excitation spectrum of order \( c/\xi(0) \), where \( c \) is a renormalized spin wave velocity. In the quantum critical region, \( g = g_c \), \( \xi = \hbar c/k_BT \), and no gap exists at \( T = 0 \). Finally, in the renormalized classical region where \( g < g_c \), the expression for the correlation length, equation 6-3, has a form similar to the corresponding classical expression, equation 6-2. In fact, the correlation length for the quantum system diverges just as it would in the corresponding classical model except that the spin stiffness \( \rho_0 \) is renormalized by quantum fluctuations and the short-wavelength cutoff is \( \hbar c/k_BT \) rather than a constant times the lattice spacing.

In the renormalized classical regime, equations 6-10 and 6-11 map directly on to a \( d = (2 + 1) \) classical model. This allowed CHN to obtain a complete expression for the van Hove scattering function. In the scaling region, the dynamical structure factor can be written in the form,
\[ S(q^*_{2D}, \omega) = \omega_0^{-1} S(q^*_{2D}) \phi(k, \nu) \]  \hspace{1cm} (6-12)

with the characteristic frequency

\[ \omega_0 \sim c_\xi^{-1} \sqrt{T/2\pi \rho_s} \]  \hspace{1cm} (6-13)

and scaling variables defined by \( \nu = \omega/\omega_0, \ k = q_{2D} \xi \). An expression for the static structure factor, \( S(q^*_{2D}) \), was found through a renormalization group analysis

\[ S(q^*_{2D}) \sim \frac{\xi^2}{1 + (2\pi \rho_s/T)^2} \frac{1 + 0.05 \ln(1 + k^2)}{1 + k^2}. \]  \hspace{1cm} (6-14)

The dynamic part of the structure factor was assumed to satisfy the dynamic scaling hypothesis, so that a reasonable form for it is

\[ \phi(k, \nu) = \frac{\gamma_k}{(\nu - \nu_k)^2 + \gamma_k^2} + \frac{\gamma_k}{(\nu + \nu_k)^2 + \gamma_k^2}. \]  \hspace{1cm} (6-15)

Expressions for the dimensionless spin wave frequency \( \nu_k \) and the width \( \gamma_k \) include four adjustable parameters: \( \gamma_0, \mu, \theta, \) and \( \delta \).

\[ \nu_k = \sqrt{3/2} \sqrt{\delta + 0.5 \ln(1 + k^2)} \cdot k \]  \hspace{1cm} (6-16)

\[ \gamma_k = \gamma_0 \sqrt{1 + \mu k^2 (1 + \theta/2 \ln(1 + k^2))^{-3/2}} \]

In order to determine these four adjustable parameters, molecular dynamics simulations of the classical rotator model were performed by Tyc, Halperin and Chakravarty.\(^1\) This is not a particularly difficult task, since a classical system was simulated. The results of these computer experiments were then fit to equations 6-12 to 6-16 to find values for the adjustable parameters. Tyc \textit{et al.} found that \( \delta = 1.05, \gamma_0 = 0.86, \mu = 1.40, \) and

\( \delta = 0.08 \) adequately fit the simulation.

The dynamic structure factor for the renormalized classical region, equations 6-12 to 6-16, resembles equation 4-9, the cross-section for damped spin waves. Qualitatively, if \( q_{2D}^2 < \xi^{-1} \) then the excitation is overdamped or diffusive in character, and if \( q_{2D}^2 > \xi^{-1} \) then the excitation is dispersive. The characteristic frequency \( \omega_0 \) is a crossover frequency where \( q_{2D}^2 = \xi^{-1} \).

To compare the QNL\( \sigma \)M cross-section to experiment, the theoretical expression for the van Hove scattering function was multiplied by the factor \( \omega (1 - e^{-\omega k a T})^{-1} \). This ensures that detailed balance is satisfied and makes the connection between classical and quantum statistics. The QNL\( \sigma \)M cross-section was then convolved with the resolution function,\(^1\) and the overall amplitude scaled to a scan at one particular temperature and energy transfer. A comparison of the QNL\( \sigma \)M prediction for the scattering and the actual neutron scattering results is shown in figure 6.9. The QNL\( \sigma \)M correctly describes both the energy and temperature dependence of the scattering remarkably well. The width of the scattering is also accounted for correctly, but this aspect of the scattering is dominated by resolution effects, so it is not a stringent test of the QNL\( \sigma \)M predictions.

The importance of the agreement between the CHN theory and the neutron scattering experimental results cannot be overestimated. The expression for \( \xi(T) \), equation 6-3, is completely determined once the experimental value for the exchange, \( J \), is known. The agreement between experiment and theory shown in figure 6.6

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1. Some subtle aspects of the convolution procedure are discussed in Appendix A.
therefore suggests that \( \text{La}_2\text{CuO}_4 \) is in the renormalized classical region, with a Neel
ordered \( T = 0 \) ground state. Agreement between the predictions of the CHN theory and
finite temperature results for \( S(Q,\omega) \) shown in figure 6.9 proves that this is indeed the
case. Thus a number of theoretical models, such as Anderson’s original RVB model
and itinerant magnetic models, are incorrect descriptions of the magnetism in
\( \text{La}_2\text{CuO}_4 \). Further, the usefulness of the QNLOM for describing the behavior of
\( \text{La}_2\text{CuO}_4 \) suggests that this general approach may be applicable for analyzing the
behavior of doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) as well.
7. Magnetism in Metallic and Superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The magnetism present in metallic and superconducting samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is by far the most interesting and important topic addressed in this thesis. Over the past 2½ years, many of the world's best physicists have been trying to understand the relationship between the superconductivity and the magnetism in the high-$T_c$ materials. The neutron scattering experiments described in this chapter have provided extensive microscopic information about the magnetism in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ which cannot be obtained using any other technique. These results would therefore seem to be crucial for understanding the physics of this system.

This chapter will examine primarily the behavior of samples with 4 different hole concentrations, $p \sim 0.02$, 0.05, 0.07, and 0.13. In section 7.1 some of the characterization measurements done on these samples are described. Energy integrating 2-axis measurements are presented in 7.2, and 3-axis experiments are discussed in section 7.3. A discussion of the relevance of these results to current theories of the superconducting state is given in chapter 8.
7.1 Sample Characterization Measurements

Table 7.1 lists some of the physical properties of five of the most important samples studied.

<table>
<thead>
<tr>
<th>Label</th>
<th>p</th>
<th>Vol(cm$^3$)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$T_0$ (K)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTT-11</td>
<td>−0.02</td>
<td>0.20</td>
<td>5.36</td>
<td>13.16</td>
<td>5.39</td>
<td>463</td>
<td>−</td>
</tr>
<tr>
<td>NTT-10</td>
<td>0.05</td>
<td>0.45</td>
<td>5.36</td>
<td>13.18</td>
<td>5.39</td>
<td>428</td>
<td>−</td>
</tr>
<tr>
<td>NTT-30</td>
<td>0.07</td>
<td>0.75</td>
<td>5.36</td>
<td>13.22</td>
<td>5.36</td>
<td>265</td>
<td>10</td>
</tr>
<tr>
<td>NTT-35</td>
<td>0.07</td>
<td>1.45</td>
<td>5.36</td>
<td>13.22</td>
<td>5.36</td>
<td>265</td>
<td>10</td>
</tr>
<tr>
<td>KOS-1</td>
<td>0.13</td>
<td>0.60</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>200</td>
<td>33</td>
</tr>
</tbody>
</table>

The techniques used to characterize the samples and the rationale for determining hole concentrations are discussed in chapter 4. It should also be noted that all samples studied were extremely uniform; oxygen and strontium concentration gradients, $\Delta y$ and $\Delta x$, were estimated to be less than 0.015 from the degree of rounding in the tetragonal-orthorhombic transition.

The positions of the samples on a schematic temperature versus hole concentration phase diagram are shown in figure 7.1.
Figure 7.1. Hole Concentration vs. Temperature Phase Diagram

Note that samples which are just barely nonsuperconducting (NTT-10) and superconducting (NTT-30 and NTT-35) have been examined. The changes in magnetic behavior which occur as \( p \) crosses the superconducting threshold will prove to be very interesting. In addition, doped samples which are far from the superconducting threshold on the insulating (NTT-11) and superconducting (KOS-1) sides are represented.

It is useful to review some of the characterization measurements done on a few of the samples more carefully. The resistivities of NTT-10, NTT-30, and KOS-1 are shown in figure 7.2. Because of the irregular shapes of these crystals, the magnitude of the resistivity is uncertain in each case to within a factor of \( \sim 2 \). Note also that the resistivity perpendicular to the \( \text{CuO}_2 \) planes in NTT-30 and KOS-1 is \( \approx 50 \) times larger than that in the planes. Such large anisotropy is typical of the highest quality single
crystals, as discussed, for example, by Preyer et al.\(^1\)

![Graph showing resistivity vs. temperature for La\(_{2-x}\)Sr\(_x\)CuO\(_4\) crystals.](image)

**Figure 7.2. Sample Resistivities**

In the p=0.05 and 0.07 samples, the resistivity shows behavior intermediate

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between that of pure single crystals of La$_2$CuO$_{4+y}$ and that of T$_c$~40K ceramics. The resistivity of these samples increases at low T, but only by a factor <4 between 250 and 5K. In addition, the p=0.07 sample, NTT-30, undergoes a superconducting transition at 10K. The p=0.13 sample becomes superconducting at 33K; above this transition it exhibits metallic behavior with dp/dT > 0.

The in-plane resistivity only will be considered now. The temperature dependence of the normal-state resistivity for NTT-30 is consistent with that predicted by the theory of weak localization in two dimensions.\(^1\) This theory predicts a decrease in conductance at low temperatures proportional to ln(T), with a prefactor that is of order e$^2$/\(\pi h\) and is independent of the conductivity itself. The resistivity for NTT-30 can be fit adequately with the ln(T) form, and the prefactor is within a factor of ~4 of e$^2$/\(\pi h\). The resistivity of NTT-10 can also be adequately fit with a ln(T) form, but for this sample the prefactor disagrees with the weak localization prediction, e$^2$/\(\pi h\), by a factor of ~50. Weak localization theory is valid only when the change in conductance due to localization effects, \(\Delta G\), is much smaller than the conductance itself. In NTT-10 \(\Delta G/G > 1\), while in NTT-30 \(\Delta G/G \approx 0.15\). It is therefore reasonable that NTT-30 exhibits a conductance which is consistent with 2-D weak localization theory while NTT-10 does not. Dedicated experiments to test the predictions of weak localization theory are underway.\(^2\) With regard to the T$_c$ = 33K sample, KOS-1, it should be mentioned that the small upturn in the resistivity of this sample just above the superconducting transition is too small to fit meaningfully to the ln(T) form. However,


\(^{2}\) Preyer, N. W., ongoing work.
it definitely does not fit the A/T + BT form predicted by Anderson and Zou\(^1\) either.

One of the most important properties of the superconducting samples which must be determined is the superconducting volume fraction. Although resistivity measurements are useful for determining \(T_c\), there is always the possibility that the resistivity is dominated by highly conductive filaments within the material, so that a sample which is predominately nonsuperconducting actually appears to be superconducting. One way to qualitatively gauge the bulk superconducting properties of a sample is through neutron depolarization measurements.\(^2\) Although this type of measurement cannot quantitatively determine the superconducting fraction, it can show whether a sample goes superconducting throughout the sample, as opposed to just on the surface. In these measurements, microscopic magnetic fields which arise from the flux excluding properties of the superconducting state depolarize a polarized neutron beam, which then causes an increase in certain modes of scattering. In the depolarization experiments done at Brookhaven, the mode of scattering which is increased from the microscopic magnetic fields has a horizontal (HF) as opposed to vertical (VF) external field on the sample. As can be seen in figure 7.2, the neutron depolarization measurements done on KOS-1 show a superconducting transition consistent with the resistivity measurements. In particular, the depolarization results indicate that the transition in KOS-1 is very sharp. Similar neutron depolarization results were obtained on NTT-30 and NTT-35. However, for these samples the neutron depolarization studies indicated that the superconducting transition was rounded.

considerably; this rounding will be addressed in the magnetization measurements described below.

Magnetization measurements were taken on a piece of dimensions 6×6×2 mm³ broken off from NTT-35 and the entire volume of KOS-1. The experiments were done in both the field cooled (FC) and zero field cooled (ZFC) configurations. Because of flux pinning effects, the volume of a sample which will completely expel flux (Meissner effect) in a FC experiment is very small for external magnetic fields greater than a few Gauss.¹ Magnetization measurements must therefore be interpreted cautiously. From ZFC flux exclusion measurements it was estimated that 80 ± 20% of both NTT-35 and KOS-1 were superconducting at 5K. The character of the superconducting transition in the piece broken off from NTT-35 may be judged from the data shown in figure 7.3, which exhibits the magnetization versus temperature taken in the ZFC configuration.

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Figure 7.3. Magnetization vs. Temperature in La$_{1.89}$Sr$_{0.11}$CuO$_{4-y}$

The magnetization of NTT-35 is denoted by the open circles, while the solid circles represent the behavior observed in a sample identical to NTT-35 which had been annealed in an oxygen atmosphere. Apparently, oxygen concentration gradients have produced a variation in $T_c$ of $\sim$5K in NTT-35. However, this spread in $T_c$ is consistent with estimates for oxygen inhomogeneity determined from the rounding in the tetragonal-orthorhombic structural phase transition. All neutron scattering experiments reported in this chapter were performed on samples in their as-grown state.

In the $T_c = 33$K superconducting sample, KOS-1, the sharpness of the transition determined from magnetization measurements was consistent with the neutron depolarization results shown in figure 7.2. The difference in the sharpness of the superconducting transition in NTT-35 and KOS-1 is easy to understand. From figure 7.1 one can see that at $p \sim 0.07$ a spread in hole concentration of $\Delta p \sim 0.01$ would cause variations in $T_c$ from 0K to $\sim 15$K; however, at $p \sim 0.13$ a spread in hole concentration of $\Delta p \sim 0.01$ would cause a variation in $T_c$ from $\sim 30$K to $\sim 35$K. It should therefore not
be surprising that KOS-1 has a sharper superconducting transition than NTT-35.
7.2 2-axis Experiments

Some of the energy integrating 2-axis measurements done on doped La$_{2-x}$Sr$_x$CuO$_{4-y}$ samples will be discussed in this section.\(^1\) The technical details of 2-axis scans are discussed in chapter 4; there it was shown that approximate measurements of the *instantaneous* spin-spin correlation function can be obtained using this type of scan. Thus the basic nature of the magnetic correlations and their length scale are the primary features of the magnetism in La$_{2-x}$Sr$_x$CuO$_4$ which have been elucidated in these measurements.

Neutron scattering experiments were done on spectrometers H7 and H4M at the High Flux Beam Reactor. All samples were mounted in the orthorhombic (h,k,0) zone, and because of twinning the (0,k,l) zone was measured simultaneously. A variety of spectrometer configurations were used in order to optimize the visibility of the signal.

Figure 7.4 shows 2-axis scans taken at low temperatures in samples with hole concentrations of p=0.02, 0.05, 0.07, and 0.13. The trajectory of these scans in momentum transfer space is depicted in figure 4.8. For all samples except KOS-1, the energy of the incident neutrons was 14.7meV; in KOS-1 scattering could only be observed if E$_i$ = 30.5 meV. The filtered 2-axis technique was employed in the scans for NTT-10 and KOS-1; pure 2-axis scans are shown for the other two samples. Since different experimental conditions were employed in each of these scans, the relative

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intensity of the scattering cannot be compared here.
Figure 7.4. 2-axis Scans in Doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$-$y$
There is an enormous amount of information in figure 7.4. First, note that doping with strontium did not destroy the Cu$^{2+}$ magnetic moments, even in superconducting samples. This experimental fact alone repudiates a number of theoretical models. Further, the transition into the superconducting state does not affect the instantaneous spin correlations, since the scattering observed above and below $T_c$ in NTT-30 is identical.

The scattering observed in all samples is to a first approximation centered around the $h = 1$ antiferromagnetic Bragg rod position. Thus the spin correlations are basically antiferromagnetic in nature. However, the superconducting samples have two peaks split off from $h = 1$ rather than a single peak centered at the antiferromagnetic Bragg peak position.\(^1\) This double peak structure is a signature of incommensurate spin correlations; it does not arise from the orthorhombic distortion, which is always less than ~0.01 r.l.u. in these samples. The double peak structure therefore represents a remarkable change in the nature of the Cu$^{2+}$ spin correlations which apparently heralds superconductivity in the system. More detailed experiments probing the incommensurate structure will be presented in section 7.3.

The length scale of the magnetic correlations will be discussed primarily in this section. Recall from equations 4-8 and 4-13 that the width of a 2-axis scan is basically inversely proportional to the magnetic correlation length of the spin system. Thus if a single Lorentzian, equation 4-13, satisfactorily fits the scattering, then the

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\(^1\) The double peak structure was independently discovered by Yoshizawa et al., J. Phys. Soc. Jpn. 57, 3686 (1988).
width extracted from this fit can be interpreted to be the inverse magnetic correlation length. In figure 7.4, the lines through the scattering observed in NTT-11 and NTT-10 are single Lorentzians convolved with the 2-axis resolution function described in chapter 4; this simple form obviously fits the scattering in these samples reasonably well.

A problem arises when one tries to find the length scale of the magnetic correlations from the double peaked scans in figure 7.4; the appropriate cross-section for this type of scattering is unknown. It is nonetheless natural to fit the double peaked scattering to the sum of two Lorentzians

\[
I(Q) \sim \frac{A}{(q - \tau_1)^2 + \kappa^2} + \frac{A}{(q - \tau_2)^2 + \kappa^2}. \tag{7-1}
\]

This is not the only form possible; as discussed in section 7.3, the double peaks could arise from a number of different spin states which would give slightly different expressions for the scattering function. For finding the approximate length scale of the magnetic correlations equation 7-1 should be sufficient, however. Indeed, as can be seen in figure 7.4, this form fits the scattering observed in NTT-30 quite well; further, fits to variations of equation 7-1 produced essentially the same results.

The temperature dependence of the pure 2-axis scattering observed in NTT-30 is shown in figure 7.5. The data were taken with \( E_i = 14.7 \text{meV} \) and the collimator configuration was 40′–40′–40′–80′.
Figure 7.5. Temperature Dependence of 2-axis Scattering in NTT-30
The scattering in figure 7.5 is flat topped with some indication of a double peaked structure. In fact, the double peaked structure is just obscured by some parasitic scattering; scans taken with $E_i = 13.7$ meV definitely have two peaks. This just illustrates once again how difficult these experiments were. The intensity of the scattering is basically independent of temperature. However, equation 4-11 shows that the range of energy integration in 2-axis scans is temperature dependent; it is therefore difficult to interpret the temperature dependence of the intensity. A detailed analysis of the temperature dependence of the scattering can only be obtained in 3-axis experiments, where the range of energy transfer that is probed can be controlled.

Consider now the temperature dependence of the scattering lineshape in figure 7.5. It is clear that the linewidth in NTT-30 is basically independent of temperature over the range probed; this is true for all Sr doped samples studied, regardless of their Sr concentration. Figure 7.6 shows the temperature dependence of $\kappa$ extracted from fits to Lorentzians in NTT-11 and NTT-30.
The scattering in figure 7.5 is flat topped with some indication of a double peaked structure. In fact, the double peaked structure is just obscured by some parasitic scattering; scans taken with $E_i = 13.7$ meV definitely have two peaks. This just illustrates once again how difficult these experiments were. The intensity of the scattering is basically independent of temperature. However, equation 4-11 shows that the range of energy integration in 2-axis scans is temperature dependent; it is therefore difficult to interpret the temperature dependence of the intensity. A detailed analysis of the temperature dependence of the scattering can only be obtained in 3-axis experiments, where the range of energy transfer that is probed can be controlled.

Consider now the temperature dependence of the scattering lineshape in figure 7.5. It is clear that the linewidth in NTT-30 is basically independent of temperature over the range probed; this is true for all Sr doped samples studied, regardless of their Sr concentration. Figure 7.6 shows the temperature dependence of $\kappa$ extracted from fits to Lorentzians in NTT-11 and NTT-30.
Figure 7.6. Temperature Dependence of $\kappa$ in Doped Samples

To a first approximation, the magnetic correlation length of all strontium doped samples is independent of temperature. This behavior is quite different from that observed in undoped La$_2$CuO$_{4+y}$. Recall from figure 6.6 that $\kappa = \xi^{-1}$ varied by a factor of 10 between 500K and 300K in these samples.

The 2-D antiferromagnetic correlation length versus hole concentration is shown in figure 7.7.
The most notable feature here is the very short length scale for the magnetic correlations in heavily doped samples; $\xi_{2D}$ is between 10Å and 20Å. Excess holes have a remarkably disruptive effect on the Cu$^{2+} - $Cu$^{2+}$ antiferromagnetic spin correlations. The line in figure 7.7, $3.8/\sqrt{p}$Å, is the average separation between the holes in the CuO$_2$ planes. Further, it was stated in chapter 2 that the superconducting coherence length, $\xi_S$, is about 15Å within the CuO$_2$ sheets. This leads to the first major conclusion of the La$_{2-x}$Sr$_x$CuO$_4$ neutron scattering experiments:

The antiferromagnetic correlation length in superconducting samples is of the order of the superconducting coherence length, and both of these quantities are comparable to the hole separation separation within the CuO$_2$ sheets.

The importance of this result cannot be overestimated. Any reasonable theory of the superconductivity in this system must also account for the magnetism, and the range of the magnetic correlations is one of the most fundamental aspects of this magnetism. The experimentally determined length scale of the magnetic correlations indicates that
theoretical calculations involving both the magnetism and the superconductivity will be difficult. This is because simple schemes which assume that the carriers reside in either a completely correlated or uncorrelated spin lattice will not work. Indeed, no physicist had even assumed that this was the correct length scale for the magnetism prior to the neutron scattering results.

Measurements probing the 2-D nature of the scattering in NTT-30 are shown in figure 7.8. In these measurements, $E_i$ was 14.7 meV and the collimation was 40'-40'-40'-80'. The scan in the top of the figure is a filtered 2-axis scan, and the bottom scan shows quasielastic ($|\Delta E|<0.5$ meV) scattering. Similar filtered 2-axis data were observed in the rest of the samples.

![Figure 7.8. 2-axis Scans Parallel to the Rod in NTT-30](image)

The filtered 2-axis rod scan observed in NTT-30 is virtually identical to the rod scan for undoped La$_2$CuO$_{4+y}$ shown in figure 6.8. The peak at $k = 0.57$ r.l.u. occurs because, as discussed in chapter 4, this is the position where $k_f$ is parallel to the 2-D rod. Consequently the scattering must be both highly inelastic and two-dimensional, characteristics of the magnetic scattering observed in La$_2$CuO$_{4+y}$. This provides
reasonable evidence that the scattering observed is actually magnetic in character; conclusive proof that this is the case will be presented in section 7.3.

The bottom scan in figure 7.8 illustrates one of the horrors that have been encountered in the course of these experiments. It would seem that the scattering in this scan is intrinsic, especially since it has the symmetry of the reciprocal lattice. That is, there is scattering centered at both $k = +0.5$ and $k = -0.5$. However, when the scan was repeated with $E_i = 13.7$ meV, scattering centered at $k = +0.4$ and $k = -0.4$ was observed. This demonstrates that the scattering shown in the bottom of figure 7.8 is not intrinsic. The reason why parasitic scattering can so easily contaminate the quasielastic signal is that the intrinsic scattering is extremely weak; further, parasitic scattering is particularly strong at quasielastic energy transfers. In general, quasielastic measurements in heavily doped $La_{2-x}Sr_xCuO_4-y$ are so prone to contamination that they cannot be used. Pure 2-axis scans which include the quasielastic component must also be interpreted cautiously.
7.3 3-axis Experiments

3-axis measurements on doped La$_{2-x}$Sr$_x$CuO$_{4-y}$ samples are presented in this section.\(^1\) The size of the instrumental resolution ellipsoid in the 3-axis configuration is typically \(~1\) meV full width at half maximum; therefore the magnetic excitations at reasonably well defined energies are measured in these scans. A schematic representation of the 3-axis resolution ellipsoid going through $S(Q',\omega)$ is shown in figure 4.11.

A detailed examination of the incommensurability first observed in the 2-axis scans will be presented here. The scattering at 300K observed in the sample which is just barely nonsuperconducting, NTT-10, is shown in figure 7.9.

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Figure 7.9. Constant-E Scans Across the 2-D Magnetic Rod in NTT-10

The scans in figure 7.9 were taken in the $E_1$-fixed configuration; as discussed in Appendix A, the intensity must therefore be multiplied by a correction factor, $\tan(\theta_A)/k_f^3$, where $\theta_A$ is the analyzer scattering angle. Thus scans at higher absolute

energy transfers have corrections which considerably reduce the experimentally measured intensity. These corrections have not been applied to the data shown. In addition, the 3-axis focusing effects described in chapter 4 have been exploited in order to boost the intensity of the intrinsic signal above the background. Therefore the position along the 2-D rod was different for each energy transfer; the positions were \( k = 1.15, 2.15, \) and 3.00 r.l.u. for energy transfers of \( E = -3.0, -9.0, \) and \(-15.0\) meV respectively.

Scans probing the temperature dependence of the scattering in NTT-10 are shown in figure 7.10.
**Figure 7.10.** Temperature Dependence of Constant-E Scans in NTT-10

In this set of scans, the spectrometer was run in the $E_F$-fixed mode, so a different correction factor must be applied.\(^1\) This correction decreases the intensity of the 9 meV scattering relative to the 3 meV scattering by a factor of \(-20\%\).

It is clear from the data in figures 7.9 and 7.10 that there is absolutely no evidence for incommensurability at any energy transfer at any temperature in this

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sample, since the peaks are all symmetric and centered about \( h = 1 \). Fits to a double peaked scattering function indicate that any possible incommensurability which may have been obscured by disorder and instrumental resolution effects is less than 0.03 Å\(^{-1}\). As can be seen in figure 7.9, the line shape at 300K does not change in width between 3 and 15 meV, and indeed this width is just that determined from the 2-axis measurements presented in section 7.2. Further, the line shape of the 3 and 9 meV scattering shown in figure 7.10 is approximately independent of temperature.

Now consider the behavior in a sample which is just barely superconducting, NTT-35. Figure 7.11 shows \( E_i \)-fixed scans taken at 300K analogous to those in figure 7.9, and figures 7.12 and 7.13 show the temperature dependence of the scattering observed in \( E_r \)-fixed scans analogous to figure 7.10.
Figure 7.11. Constant-E Scans Across the 2-D Magnetic Rod in NTT-35
Figure 7.12. Temperature Dependence of Constant-E Scans in NTT-35
Figure 7.13. Temperature Dependence of Constant-E Scans in NTT-35

A number of very interesting features may be seen in the data of figures 7.11–7.13. First, $S(Q',\omega)$ in the superconducting sample clearly exhibits peaks which are split off from the (1,0,0) antiferromagnetic peak position. At 300K this incommensurability is visible at 9 and 15 meV, and at lower temperatures the incommensurability can be seen at 1.5, 4.5, and 6 meV as well. The 3-axis scans shown here definitively confirm the 2-axis results described in section 7.2; incommensurate spin correlations occur only in superconducting samples.

The incommensurability is not clearly resolved at all energies, temperatures and experimental configurations; this occurs at least partly because the temperature dependent inelastic background and instrumental resolution effects can easily obscure
the intrinsic signal. That the double peak structure becomes more clearly resolved at lower temperatures in the 1.5 and 4.5 meV scattering nonetheless appears to be intrinsic. One might want to interpret this behavior as a transition into an incommensurate state; more experiments are needed to resolve this issue, however.

The 3-axis scattering observed in the $T_c = 33$ K sample, KOS-1, will be discussed now. $E_i$-fixed scans with $E_i = 30.5$ meV are shown in figure 7.14, where the scattering normalized by sample volume in both NTT-2 ($\text{La}_2\text{CuO}_4$) and KOS-1 ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) are shown.

![Figure 7.14](image)  

**Figure 7.14.** Constant-E scans in $\text{La}_2\text{CuO}_4$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

Two features are immediately evident. First, it is clear that KOS-1 has incommensurate spin correlations, just like the $T_c = 10$ K superconducting samples.
The magnitude of the incommensurability also does not change much when the hole concentration is increased. Second, the integrated $\langle \text{dQ} \rangle$ intensities of the insulating and superconducting samples are identical within experimental errors. This is strong experimental evidence that the Cu$^{2+}$ moments persist in superconducting La$_{2-x}$Sr$_x$CuO$_4$.

Scans at a number of different energy transfers are shown in figure 7.15. The temperature was 150K, and the spectrometer was run in the $E_f$–fixed configuration at $E_f = 13.7$ meV.
Figure 7.15. Constant-E scans in La$_{1.85}$Sr$_{0.15}$CuO$_4$

The scattering at all energies except possibly 3 meV is flat topped; however, when the background is clean it is possible to see the double peak structure clearly. Comparing data shown in figures 7.11 and 7.15, it is obvious that the response at high energies in $T_c = 10$K and $T_c = 33$K samples are similar in spite of the difference in deccuting transition temperatures.

The dependence of the scattering at 6 meV and 12 meV in KOS-1 is

or the 12 meV data the spectrometer was run in the $E_f$-fixed
mode with $E_f = 13.7$ meV. For the 6 meV data the spectrometer was run with $E_f$ fixed at 30.5 meV. These two different configurations were used in order to optimize the visibility of the intrinsic scattering.

\[ \text{KOS-1, La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \]

\[ E = 12 \text{ meV} \quad \text{E = 6 meV} \]

\[ 300 \text{K} \quad 300 \text{K} \]

\[ (h, -1.8, 0) \quad (h, -1.2, 0) \]

\[ 13.7E_f, 40-80^3 \quad 30.5E_f, 40^2-80^2 \]

\[ 150 \text{K} \quad 150 \text{K} \]

\[ \text{Intensity (counts/20 min.)} \quad \text{Intensity (counts/14 min.)} \]

\[ 10 \text{K} \quad 5 \text{K} \]

\[ \text{Intensity (counts/10 min.)} \quad \text{Intensity (counts/7 min.)} \]

\[ 0.5 \quad 0.5 \]

\[ 1 \quad 1 \]

\[ 1.5 \quad 1.5 \]

\[ h \quad h \]

\[ \text{Figure 7.16. Temperature Dependence of the Scattering in La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \]

The lineshape of the 6 meV scattering is basically independent of temperature, but the intensity clearly decreases as the temperature is decreased. The 12 meV scans have some phonon contamination for $h>1.1$. However, the intensity for $h<1.1$, which is magnetic in origin, appears to be temperature independent.
The 3-axis and 2-axis measurements on the nonsuperconducting and superconducting samples presented above provide clear evidence for the second major conclusion of the La_{2-x}Sr_xCuO_4 neutron scattering experiments:

*Nonsuperconducting samples exhibit short range commensurate antiferromagnetic order, while superconducting samples exhibit short range incommensurate antiferromagnetic order.*

Since the incommensurability appears to be correlated with the superconductivity, it is probably related to the motion of the charge carriers. It should be noted that very few theoretical models had accounted for incommensurate spin states prior to their experimental discovery; consequently most of the theoretical models conceived before this experimental discovery are inadequate.

The current knowledge of the nature of the incommensurate spin state should be clarified. In figure 7.17 the geometry of the scattering for two different spin states which would produce the observed double peak scan are shown.
Figure 7.17. Incommensurate Scattering Geometries

The experiments described here cannot distinguish between the two incommensurate geometries shown in figure 7.17, since scans were done only in the (1,0,0) direction. Preliminary measurements were carried out in the [010] zone in an attempt to map out the geometry of \( S(Q,\omega) \) in the plane defined by (1,0,0) and (0,0,1). However, in the [010] zone the background increases by a factor of \(-3\); consequently no convincing data was obtainable in a reasonable amount of time.

To get an idea of the spatial spin correlations which might cause
incommensurate scattering, consider a simple 1-D chain of spins where
\[ S_z(x) = S_0 \cos\left(\frac{\pi + \Delta}{a}x\right). \] If \( \Delta = 0 \), then scattering at the antiferromagnetic Bragg positions \( q = \pm \frac{\pi}{a}, \pm \frac{3\pi}{a}, \text{ etc.} \) would be observed. If \( \Delta \neq 0 \), then the scattering intensity would be

\[
I(q) = \int_{-\infty}^{+\infty} e^{i q x} S_z(x) S_z(0) dx
\]

\[
I(q) = \int_{-\infty}^{+\infty} e^{i q x} \left[ e^{i \frac{(\pi + \Delta)}{a}x} + e^{-i \frac{(\pi + \Delta)}{a}x} \right] dx
\]

\[
I(q) = \sum_{n = \pm 1} \delta\left(q + \frac{(\pi + \Delta)}{a} - \frac{2\pi n}{a}\right) + \delta\left(q - \frac{(\pi + \Delta)}{a} - \frac{2\pi n}{a}\right)
\]

Thus scattering will occur at \( q = \frac{\pi + \Delta}{a} \) and \( \frac{\pi - \Delta}{a} \) instead of \( \frac{\pi}{a} \). The phase angle, \( \Delta \), for the incommensurate scattering observed in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) can be easily calculated from the splitting observed in figure 7.4. For NTT-30, \( \frac{\Delta}{a} \sim 0.1 \text{Å}^{-1} \) which implies that \( \Delta \sim 0.1 \text{Å}^{-1} \times 3.8 \text{Å} \times \frac{57^\circ}{\text{rad}} \sim 20^\circ \).

Some of the real space spin configurations which might produce incommensurate scattering\(^1\) are shown in figure 7.18.

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Figure 7.18. Incommensurate Spin Configurations

The state on the upper left is known as a canted state, and the states on the upper right and lower left are known as spirals. In the configuration on the lower right, the isotropic spin liquid state, the spins partially point out of the plane. In all of these spin states, nearest neighbor spins must be rotated by \(-20^\circ\) in order to produce the experimentally observed incommensurability.

In order to gain some insight into the temperature and energy dependence of the spectral distribution, the 1-D integrated intensity of the scattering has been calculated. That is, the area under the curves shown in figures 7.9–7.16 have been found. It should be emphasized that a true comparison of the spectral weight can only be obtained from integrals over one Bril’ouin zone in Q space; however, since the
complete geometry of $S(Q',\omega)$ is not known, the results from 1-D integrations only are presented. This approximation should not change the results qualitatively.

In figure 7.19 the integrated intensity versus energy transfer at 300K in NTT-10 and NTT-35 is shown. Corrections for the $\tan(\theta_A)/k_f^3$ factor and magnetic form factor have been included in this calculation, and the intensity has been normalized by the sample volumes.

![Figure 7.19](image)

**Figure 7.19.** Integrated $\langle dQ \rangle$ Intensity vs. Energy Transfer for NTT-10 and NTT-35

The large energy scale for the magnetic fluctuations observed in undoped La$_2$CuO$_4$ is also present in doped samples; the scattering at 6 and 15 meV have comparable integrated intensities. As can be seen in figure 7.15, the scattering in KOS-1 also has the same large energy scale. From the arguments given in chapter 4, this means that the Cu$^{2+}$–Cu$^{2+}$ spin system in La$_{2-x}$Sr$_x$CuO$_4$ is fluctuating rapidly compared to conventional antiferromagnets. It should be mentioned that the low temperature spin glass-like transition has been probed in NTT-10 by Sternlieb *et al.* When this transition occurs, an intense quasielastic ($|\Delta E|<0.5$ meV) component appears at
antiferromagnetic rod positions.¹

The temperature dependence of the integrated intensity is summarized in figure 7.20. Note that the data in this figure were taken under a variety of experimental conditions; consequently the magnitude of the intensities cannot be compared at different energy transfers and between the three samples.

¹ Sternlieb, B., et al., private communication.
Figure 7.20. Integrated $\int dQ$ Intensity vs. Temperature
There are a number of interesting features in the data of figure 7.20. First, consider the temperature dependence of the scattering at 6 meV in NTT-35 and 12 meV in KOS-1. At these particular energies the intensity is nearly temperature independent over the entire range 5k<T<300K. The lack of temperature dependence is very unusual, and in fact La$_{2-x}$Sr$_x$CuO$_4$ appears to be the first antiferromagnet where this phenomenon has been encountered.

In order to illustrate how strange the temperature independent scattering intensity really is, the Bose occupation scattering factor for +6 meV excitations, $1 + 1/(e^{\omega k_B T} - 1)$, is shown in the inset of figure 7.20. As can be seen in equations 4-9 and 4-23, the temperature dependence of the intensity for conventional phonons and magnons follows the Bose factor, since the line shape is independent of temperature. The mystery in the temperature independent behavior is that the intensity does not change when the temperature is varied from above to below the characteristic energy of the magnetic excitation. It would therefore seem as if another energy scale exists in this system in addition to the thermal energy scale.

As a cross check to test this behavior, scans were performed at both +6 meV and -6 meV on NTT-35. As can be seen in figure 7.12, the scattering at -6 meV decreases as the temperature is lowered. This is in accord with detailed balance,\(^1\) which states that

$$S(Q',-\omega) = e^{-\beta \omega} S(Q',\omega) \quad (7-3)$$

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where $\beta = 1/k_B T$. In figure 7.12 the line through the $-6$ meV scattering was actually calculated from a fit to the $+6$ meV scattering scaled by the detailed balance factor. Consequently the measured scattering is intrinsic with little or no contamination from parasitic scattering events.

Important differences between superconducting and nonsuperconducting samples exist in the temperature dependence of the integrated intensity. At lower energy transfers, the intensity decreases with decreasing temperature in the superconducting samples, while it increases with decreasing temperature in the nonsuperconducting sample. For the superconducting samples, figure 7.20 shows that the integrated intensity of the 4.5 meV scattering in NTT-35 and the 6 meV scattering in KOS-1 both decrease as the temperatures is lowered. In addition, the temperature dependence of the integrated intensity at 3 and 9 meV in KOS-1 is similar to that at 6 meV. On the other hand, the integrated intensity at 3 and 6 meV for the nonsuperconducting actually increases as the temperature is lowered. If one considers the behavior of all samples, there is only one reasonable explanation for this behavior: gaps in the spin excitation spectrum of order $\sim 5$ meV and $\sim 10$ meV open up in $T_c \sim 10$K and $T_c \sim 33$K samples respectively, while no gap appears in nonsuperconducting samples. Further, the weak coupling BCS quasiparticle gaps for the two samples, $2\Delta = 3.5 k_B T_c$, are $\sim 3$ meV and $\sim 10$ meV, respectively. Although fluctuation effects,\(^1\) anisotropy in the gap,\(^2\) and strong coupling effects may effectively increase the actual gap value considerably, it is tempting to associate the magnitude of the spin excitation gap with the magnitude

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of the superconducting quasiparticle gap.

A gap in the spin excitation spectrum comparable to the quasiparticle gap apparently opens up in superconducting samples, while no gap appears in nonsuperconducting samples.

This is the third major conclusion of the La$_{2-x}$Sr$_x$CuO$_4$ neutron scattering experiments. This result not only provides another major experimental clue about the nature of the Cu$^{2+}$–Cu$^{2+}$ spin correlations, it also is the first direct evidence connecting the superconductivity and the magnetism.

The gap data for KOS-1 are cleanest, so only this data will be considered now. There are two features of this data which are surprising. First, the gap develops well above $T_c$, which suggests that the existence of a gap in the spin excitations is a prerequisite for the superconductivity. Analogous precursor effects which set in at $\sim$150K have been observed in NMR$^1$ experiments in both the La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_y$ systems. Second, the intensity of the magnetic scattering decreases by only $\sim$60% for energies less than the BCS quasiparticle gap value. There are a number of explanations for this behavior. The low energy magnetic scattering may arise from parts of the sample (say $\sim$40%) which do not become superconducting. This scenario is inconsistent with the flux exclusion experiments done on the sample, however.

Another possibility is that the gap is just smeared; such an effect would not be surprising given the disordered nature of the system. Finally, it may turn out that the

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1. Imai, T., et al., submitted to Phys. Rev. B.
spin excitation gap does not open up over all regions of $k^*$ space, much like the quasiparticle gap in $p$ and $d$-wave superconductors. A detailed discussion of this explanation will be given in chapter 8.

Unfortunately, polarized neutron scattering experiments, which could establish definitively that the 3-axis signals presented in this section were magnetic, could not be done because the signal is too weak. Therefore two other methods were used to confirm the magnetic origin of the scattering in NTT-35.

In the first cross check, scans across the $(1,k,0)$ and $(3,k,0)$ rod positions with the energy transfer set at 6 meV were performed. The data for this check are shown in figure 7.21.

![Figure 7.21](image)

**Figure 7.21.** Scans Across the $(1,k,0)$ and $(3,k,0)$ Magnetic Rods in NTT-35

Now if the incommensurate structure originated from phonon scattering the signal would have increased roughly as $Q^2$, assuming that the dynamic structure factor for the phonon scattering, equation 4-22, were approximately constant. A scan across the $(3,k,0)$ position would therefore have shown a double peak structure ~9 times more
intense than the equivalent scan at the $(1,k,0)$ position. On the other hand, if the scattering is magnetic in origin, due to the Cu$^{2+}$ antiferromagnetic form factor the scattering intensity would decrease by a factor of $-0.4$ in going from the $(1,k,0)$ to $(3,k,0)$ rod. The dashed line in figure 7.21 is the $(1,k,0)$ rod data scaled by 0.4. Clearly the data are consistent only with a magnetic origin for the scattering. Moreover, this result demonstrates that virtually all of the double peak signal is magnetic; this is information that could not easily be obtained from polarized neutron scattering measurements.

In the second cross check, a 6 meV scan in which the momentum transfer was scanned up the 2-D Bragg rod position was performed. The data are shown in figure 7.22.

![Figure 7.22. 3-axis Scans Parallel to the Rod in NTT-35](image)

It is clear that the scattering at this energy is independent of $k$, thus demonstrating that the spin correlations are two dimensional. The 2-D character of the double peak scattering was indirectly proven using 2-axis techniques in figure 7.8; the data presented here show this aspect of the scattering more convincingly. This 2-D nature
of the scattering provides further evidence that the signal is magnetic, since the
dynamic magnetic signal in undoped \( \text{La}_2\text{CuO}_4 \) was definitively established to be 2-D
in character in chapter 4, while the low energy phonon modes have fully 3-D
dispersion relations.
8. Relationships Between Magnetism and Superconductivity

In the previous chapter, three aspects of the magnetism in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were elucidated in the neutron scattering experiments:

(1) The antiferromagnetic correlation length in superconducting samples is of the order of the superconducting coherence length, and both of these quantities are comparable to the hole separation within the CuO$_2$ sheets.

(2) Nonsuperconducting samples exhibit short range commensurate antiferromagnetic order, while superconducting samples exhibit short range incommensurate antiferromagnetic order.

(3) A gap in the spin excitation spectrum comparable to the quasiparticle gap apparently opens up in superconducting samples, while no gap appears in nonsuperconducting samples.

The first three sections of this chapter will examine the consequences of these experimental discoveries, and the last section will discuss possible future experiments in this field.
8.1 Consequences of the Short Magnetic Correlation Length

The discovery that superconducting samples have short range magnetic correlations which are of the order of the superconducting coherence length caught most physicists by surprise. Many had thought that the magnetic moments would be destroyed at these strontium concentrations. Among those who believed that the magnetic moments would persist, some had assumed that the correlations would exist over larger length scales, but most had no ideas or predictions at all about this fundamental aspect of the system.

Some insight into the reasons why the magnetic correlations have a $\xi_{2D} - 15\text{Å}$ length scale may be obtained by considering how doping destroys antiferromagnetic correlations in a classical spin system.\(^1\) As discussed in chapter 3, in a two band model of the magnetism excess holes will frustrate Cu–Cu antiferromagnetic bonds. In the isostructural material $K_2Cu_yMn_{1-y}F_4$, the Cu magnetism is lost at $y \sim 0.8$, which corresponds to a bond concentration of $x = 0.36$.\(^2\) This is much larger than the strontium concentration where antiferromagnetic order is destroyed in $La_{2-x}Sr_xCuO_4$, $x \sim 0.02$. Some of the discrepancy might be accounted for by quantum effects and the strength of the ferromagnetic frustration,\(^3\) but the key difference between $K_2Cu_yMn_{1-y}F_4$ and $La_{2-x}Sr_xCuO_4$ appears to be that the holes are mobile in $La_{2-x}Sr_xCuO_4$. Qualitatively, it is clear that a mobile hole will be more effective than


a static hole in destroying the antiferromagnetic order, since it will be able to destroy more than one bond as it moves around.

Although it is clear that the hole carriers are responsible for destroying the antiferromagnetic spin correlations, real quantitative predictions of the 2-D magnetic correlation length in heavily doped samples have not been made. At this point, it is probably better to use the experimentally observed 2-D magnetic correlation length as input into theoretical models of the superconductivity, rather than trying to predict this quantity. This has been the approach of, for example, Birgeneau et al.\textsuperscript{1} and Lee\textsuperscript{2}.

\textsuperscript{2} Lee, P. A., preprint.
8.2 Superconductivity and Incommensurate Spin States

The incommensurate spin state discovered in the neutron scattering experiments is most likely a prerequisite for superconductivity. Whether the incommensurate spin state should be viewed as resulting from an incommensurate spin density wave (SDW),\textsuperscript{1} as a frustrated state of predominately localized spins,\textsuperscript{2} or as a spiral state arising from the motion of hole carriers\textsuperscript{3} is one of the issues which must be addressed.

In the SDW picture, an incommensurate spin state occurs if the wave vector of the spin density wave follows the Fermi wave vector with doping rather than being pinned to the lattice vector. Figure 8.1 illustrates a possible 2-D Fermi surface for doped La$_{2-x}$Sr$_x$CuO$_4$.

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Figure 8.1. 2-D Fermi Surface of La$_{2-x}$Sr$_x$CuO$_4$

Figure 8.1 is similar to figure 3.3, except that doping with Sr has caused the electron Fermi square to shrink in size. Now the wave vector of an SDW in the La$_2$CuO$_4$ system would span the Fermi surface like $k'_0$ does in figure 8.1. When the system is doped, the wave vectors of any spin density waves will become both larger and smaller; wave vectors $k'_1$ and $k'_2$ in figure 8.1 illustrate this phenomenon. Incommensurate scattering would then result. Note that the wave vectors which are perpendicular to $k'_0$ also span the Fermi surface, so the itinerant picture would produce scattering similar to the four rods of scattering shown in figure 7.17. Arguments against an itinerant description of the magnetism in La$_{2-x}$Sr$_x$CuO$_4$ have been given in chapter 3; the scenario described above may nonetheless be a useful way to think about the incommensurability.

An alternative point of view to the itinerant picture is that the Cu$^{2+}$ moments are
primarily localized on Cu sites as the result of electron–electron correlation effects. In a localized picture, mechanisms by which doped holes produce an incommensurate type of structure will most likely be related to either frustration or hole motion. Either four rods of scattering or a ring of scattering can be produced by localized incommensurate spin states.¹

The nature of a frustration² induced incommensurate has already been discussed in chapter 3. The idea is that a hole on an oxygen site will cause the Cu–Cu antiferromagnetic bond to become ferromagnetic. Frustration induced by the ferromagnetic bond will then cause neighboring spins to reorient into the spiral-like structure shown in figure 3.9. Although the scattering function for such a spin state has not been calculated, it is likely that it will be incommensurate.

Hole motion³ could induce an incommensurate Cu²⁺ spin state through an extension of the spin flipping scenario discussed in chapter 3. There it was argued that a mobile hole carrier in a single band Hubbard model would leave a wake of flipped Cu²⁺ spins as it moved through an antiferromagnetically ordered lattice. An illustration of this process was shown in figure 3.6. The reason why spin flipping occurs is that the Pauli exclusion principal only allows holes with spin opposite to that of neighboring sites to move. As illustrated in figure 8.2, this is no longer true when the spin configuration is incommensurate.

¹ Kane, C. L., et al., preprint.
Figure 8.2. Motion of Holes in Antiferromagnetic and Incommensurate Spin States

If the underlying Cu$^{2+}$ spin state is incommensurate, it is possible for both of the spins to move to a neighboring site. This is because both spins now have a finite overlap with the empty states on neighboring sites. Thus holes in an incommensurate spin state will be able to move without leaving a trail of flipped spins, so their mobility will increase.

Because of the apparent correlation between superconductivity and incommensurate spin states, it is tempting to associate the incommensurate spin state with an increased mobility of the hole carriers, which in turn may be necessary for the superconductivity. One should be cautious, however. There are many other processes which can also increase the mobility of the holes. For example, next nearest neighbor hopping processes do not leave trails of flipped spins, even if the Cu$^{2+}$ spin state is antiferromagnetic. Further, the applicability of single band Hubbard models is an
unresolved issue. This approach nonetheless seems very promising.
8.3 Superconductivity and Gaps in the Spin Excitation Spectrum

The discovery that the spin excitations in La$_{2-x}$Sr$_x$CuO$_4$ form a gap which is comparable in magnitude to the quasiparticle gap is in some ways not surprising. This is because in conventional s-wave superconductors magnetic exchange interactions will break up the Cooper pairs if there is sufficient overlap between the magnetic ions and the superconducting carriers.\(^1\) Basically, the antiparallel spin correlations of the Cooper pairs in the s-wave superconducting state prevent the carrier-magnetic moment interaction from entering as favorably as it does in the normal state. A simple mechanism which might prevent the moments from destroying the superconductivity is if a gap appears in the spin excitation spectrum. On the other hand, the magnetic moments may affect the superconducting state found in La$_{2-x}$Sr$_x$CuO$_4$ in a different way than they affect the superconductivity in conventional materials; analogies like this must therefore be viewed with caution.

At least two theories\(^2\) which predicted gaps in the spin excitations were developed prior to the experiments described in chapter 7. Not all features of the actual spin gap present in La$_{2-x}$Sr$_x$CuO$_4$ were correctly predicted by these theories, however. The most glaring discrepancy is that the theories predicted that the spin excitation gap would collapse at $T_c$. Instead, the experimentally determined spin excitation gap collapses well above $T_c$.

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An interesting possibility is that the spin excitation gap is anisotropic in momentum space. In this scenario, the fact that the intensity of the magnetic scattering shown in figure 7.20 only decreases by ~60% for energies less than the quasiparticle gap would be intrinsic. The simplest way how this could occur is if the magnetic excitations at either the (1,k,0) rod or (0,k,1) rod only developed a gap. Because of twinning the scattering shown in figure 7.20 would therefore decrease by ~50%, which is consistent with the experimental results. Given the correlation between the magnitudes of the spin excitation gap and the superconducting quasiparticle gap, a natural conjecture is that both gaps have the same symmetry in momentum space. Experimentally, the symmetry of the quasiparticle gap is unresolved. Some NMR studies\(^1\) have suggested that the quasiparticle gap has nodes. Further, Raman scattering\(^2\) experiments on YBa\(_2\)Cu\(_3\)O\(_7\) suggest that a continuum of electronic states exists down to zero energy. On the other hand, measurements of the London penetration depth\(^3\) seem to favor s-wave pairing; however, the interpretation of these results is still controversial.\(^4\) It may be possible to quantitatively test whether both the spin excitation and quasiparticle gaps have the same symmetry in future neutron and light scattering experiments.

The appearance of a gap in the spin excitations at a well defined temperature

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above $T_c$ suggests that a phase transition occurs in the Cu$^{2+}$ spin lattice which is independent of the superconductivity. An appealing explanation of the gap and the incommensurability is that they are both signatures of the new magnetic state. However, the incommensurability can be resolved at 300K at some energy transfers, while the gap appears at ~100K. This scenario would therefore appear to be unlikely. Closer examination of figures 7.12–7.14 suggests a possible resolution to this inconsistency. The key observation is that the scattering at low energy transfers does not show signs of incommensurability until the temperature is lower than ~150K. The incommensurate spin correlations observed at 300K for higher energy transfers may then just be precursor effects analogous to the spin wave-like excitations observed above the Neel temperature in ordinary antiferromagnets. In fact, a change in the spin configuration is the most plausible explanation for the appearance of a gap, since there is no evidence that the spin Hamiltonian has changed at this temperature. It may turn out that the superconductivity appears only after the copper moments have ordered in a remarkable new state.
8.4 Future Directions

The overall features of the magnetism in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been elucidated by the experiments described in this thesis. There are, however, many topics in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system which should be investigated further. A partial list of these topics is given below:

(1) The complete geometry of the incommensurate spin state must be determined.

(2) Experiments should be performed to determine definitively whether the appearance of incommensurability and a gap in the spin excitations occur simultaneously.

(3) Additional samples should be studied to determine the exact relationship between $T_c$ and the magnitude of the spin excitation gap.

(4) The spin freezing transition should be investigated more thoroughly.

(5) Experiments on samples where the hole concentration has been varied through the superconducting threshold by reduction and oxidization should be performed.

In addition, experiments on the other high-$T_c$ superconductors should be done to determine which features of the magnetism are universal and which are not.
Appendix A: Technical Aspects of Neutron Scattering Experiments

This appendix describes some of the important experimental details of the neutron scattering technique. It is far from complete, however. For more information see the research memorandums of the Brookhaven neutron scattering group.

In A.1 the correction factors for $E_i$-fixed and $E_f$-fixed scans will be reviewed. Pyrolytic graphite filters are described in A.2, and the instrumental resolution under a variety of spectrometer conditions is given in A.3. Finally, 3-axis and 2-axis fitting programs are described in A.4 and A.5 respectively.
A.1 Correction factors for $E_i$– and $E_f$–fixed Scans

The correction factor for $E_i$–fixed scans was calculated by Chesser and Axe.\textsuperscript{1} To a first approximation, the data points in a scan should be multiplied by

$$ R = \frac{\tan(\theta_A)}{k_f^3} \quad (A-1) $$

to get the intrinsic intensity. Here $\theta_A$ is the analyzer scattering angle and $k_f$ the final neutron momentum. Corrections for the efficiency of the detector and monitor are included in this expression. The energy dependence of the analyzer crystal reflectivity has not been included; however, this is not a large correction for most scans.

The correction factor for $E_f$–fixed scans was determined by Cowley \textit{et al.}\textsuperscript{2} This factor arises from the energy dependence in the efficiency of pyrolytic graphite filters. It is more convenient to list this correction factor in a table; data points at various energy transfers are multiplied by $R$ to get the intrinsic intensity.

\footnotesize

### TABLE A.1. $E_f$-fixed Correction Factors

<table>
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<th>$E_f$ = 14.7 meV</th>
<th>$E_f$ = 30.5 meV</th>
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</table>

It turns out that the corrections for $E_f$-fixed scans are usually smaller than those for $E_f$-fixed scans. Consequently this mode is used more frequently.
A.2 Pyrolytic Graphite Filters

Pyrolytic graphite filters are used extensively in neutron scattering experiments. In order to understand their purpose, one must consider how a neutron beam is monochromatized. Recall that the Bragg condition is

\[ 2k \sin(\theta) = Q \quad \text{(A-2)} \]

From this equation, one can see that when the monochromator crystal is graphite (002), neutrons with wave vectors that are multiples of the (002) wave vector will diffract off the crystal from (004), (006), etc. Bragg peaks. Further, they will all have the same Bragg angle. This is higher order contamination of the neutron beam.

The remarkable property of pyrolytic graphite filters is that they allow nearly complete transmission of neutrons with certain wave vectors, while blocking out the higher order contamination.¹ These filters are therefore placed in the neutron beam either after the monochromator (E₁—fixed scan) or analyzer (E₂—fixed scan) in order to remove the higher order contamination. It turns out that for neutron energies of 14.7 meV and 30.5 meV the transmission percentage for higher order neutrons is particularly small, while the primary harmonic transmission is still quite large. This is why almost all of the scans in this thesis were done with these particular neutron energies.

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¹ Shapiro, S. M., Chesser, N. J., Nucl. Instr. and Meth. 101, 183 (1972).
A.3 Instrumental Resolution Characteristics

Characteristics of the instrumental resolution function are listed in table A.2 for a number of important spectrometer conditions. The energy resolution (in meV) and the momentum resolution (in Å⁻¹) out of the scattering plane are denoted by $E_{\text{res}}$ and $Q_{3\text{res}}$, respectively. The projection of the resolution ellipsoid on the scattering plane is also given. For this quantity, the length of the primary axes, $Q_{1\text{res}}$ and $Q_{2\text{res}}$, and the angles that these axes make with respect to $Q$, $\theta_1$ and $\theta_2$, are given. Note that $\theta_1$ and $\theta_2$ are defined to be positive for clockwise rotations. All quantities are full widths at half maximum (FWHM). The spectrometer is assumed to be in the $E_T$-fixed mode, and $Q$ is assumed to be 1Å⁻¹.

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<th>$E_T$</th>
<th>Collimation</th>
<th>$\Delta E$</th>
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<th>$Q_{1\text{res}}$</th>
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A.4 3-Axis Fitting Programs

Programs for convolving the 3-axis resolution function with a theoretical lineshape for comparison to experimental scans have been developed at Brookhaven National Laboratory. The resolution function is calculated using the Cooper-Nathans formalism,\(^1\) and a numerical calculation of the integral in equation 4-30 is performed. Versions of these programs that have been rewritten in the C programming language for use with c-plot software are in the MIT x-ray group vax under the filenames /usr/tom/plot_func/constE.5.c and /usr/tom/plot_func/constQ.5.c.

Details about this program may be found in Brookhaven research memorandums; there is one aspect of the program which should be elaborated on here, though. In performing the four dimensional integration over momentum-energy transfer space, the trapezoidal rule is applied. Because there are four dimensions to be integrated over, the step size is normally kept rather large in order to reduce the number of numerical operations performed by the computer. This usually does not cause problems; however, for the work on La\(_2\)CuO\(_4\) it turned out that the integral over momentum transfer perpendicular to the scattering plane must have a mesh much finer than the norm. As an example, consider the mesh size for 8 meV magnons with velocity 800 meVÅ. The \(q\) for this excitation is then 0.01 Å\(^{-1}\), so an appropriate mesh size should then be at least ~0.25 of this value, 0.0025 Å\(^{-1}\). From table A.2 it can be seen that the integration over the out of plane momentum transfer must then have at least ~\((2\times0.106\ Å^{-1})/0.0025\ Å^{-1}\) = 85 steps in order to integrate over 2 full widths of the

\(^1\) Cooper, M. J., Nathans, R., Acta Cryst. 23, 357 (1967).
resolution ellipsoid. This is much larger than the number of steps that are usually used for this integration, \(-8-16\).
A.5 2-axis Fitting Programs

As discussed in chapter 4, the convolution of 2-axis scans involves integrations over the momentum transfer in directions perpendicular to the 2-D Bragg rod and out of the scattering plane. A simple function which can be used to model the instrumental resolution is a Gaussian

\[ R(R') = \frac{\ln 2}{\pi w_h w_z} e^{-\ln 2\left(\frac{k_x^2}{w_x^2} + \frac{k_y^2}{w_y^2}\right)} \tag{A-3} \]

Here \( w_h \) and \( w_z \) are the half widths at half maximums for the resolution function perpendicular to the rod and out of the scattering plane respectively. For \( \text{La}_2\text{CuO}_4 \) with \( a^* = c^* = 1.17 \text{Å}^{-1} \) and \( E_t = 14.7 \text{ meV} \), these turn out to be \( w_h \sim 0.013 \text{ r.l.u.} \) and \( w_z \sim 0.045 \text{ r.l.u.} \) respectively.

The convolution integral for a Lorentzian is

\[ I(q) = \frac{\ln 2}{\pi w_h w_z} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\ln 2\left(\frac{k_x^2}{w_x^2} + \frac{k_y^2}{w_y^2}\right)} \left(\frac{\text{AMP}}{(q_h - k_h)^2 + (q_z - k_z)^2 + \alpha^2}\right) dk_h dk_z. \tag{A-4} \]

After making the substitution \( k_i = \alpha_i w_h/\sqrt{\ln 2} \) equation A-4 becomes

\[ I(q) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-(\alpha_x^2 + \alpha_y^2)} \left(\frac{\text{AMP}}{(q_h - \alpha_h w_h/\sqrt{\ln 2})^2 + (q_z - \alpha_z w_z/\sqrt{\ln 2})^2 + \alpha^2}\right) d\alpha_h d\alpha_z. \tag{A-5} \]

This integral may be easily evaluated using Hermitian quadrature

\[ \int_{-\infty}^{+\infty} e^{-x^2} f(x) dx = \sum_i H_i \cdot f(x_i) \tag{A-6} \]
Table A.3 gives parameters for twelve point Hermitian quadrature.

<table>
<thead>
<tr>
<th>±x_i</th>
<th>H_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3142404</td>
<td>0.5701352</td>
</tr>
<tr>
<td>0.9477884</td>
<td>0.2604923</td>
</tr>
<tr>
<td>1.5976826</td>
<td>0.0516080</td>
</tr>
<tr>
<td>2.2795071</td>
<td>0.0039054</td>
</tr>
<tr>
<td>3.0206370</td>
<td>0.0000857</td>
</tr>
<tr>
<td>3.8897249</td>
<td>0.0000003</td>
</tr>
</tbody>
</table>

Twelve point Hermitian quadrature is accurate as long as \( \kappa \) is greater than \( \sim 40\% \) of \( w_h \). If \( \kappa \gg w_h \), then the integration in the \( k_h \) direction may be omitted.
Appendix B: Crystal Properties

The properties of the La$_{2-x}$Sr$_x$CuO$_{4-y}$ crystals studied at Brookhaven National Laboratory are summarized in table B.1. Sample characterization methods are described in chapter 4. Definitions for this table include: $x =$ strontium concentration, $p =$ estimated hole concentration, $v =$ volume, $a$, $b$, $c =$ lattice constants at 300K, $T_0 =$ structural phase transition temperature, $T_N =$ Neel temperature, and $T_c =$ superconducting phase transition temperature.

<table>
<thead>
<tr>
<th>Label</th>
<th>x</th>
<th>p</th>
<th>v(c.c.)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>$T_0$(K)</th>
<th>$T_N$(K)</th>
<th>$T_c$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTT-2</td>
<td>0</td>
<td>~0.01</td>
<td>0.40</td>
<td>5.360</td>
<td>13.150</td>
<td>5.408</td>
<td>503</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>NTT-3</td>
<td>0</td>
<td>&gt;0.01</td>
<td>0.40</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>499</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MIT-10</td>
<td>0</td>
<td>0.008</td>
<td>1.60</td>
<td>5.359</td>
<td>13.152</td>
<td>5.405</td>
<td>503</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>NTT-7</td>
<td>0</td>
<td>0.008</td>
<td>~2</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>515</td>
<td>245</td>
<td></td>
</tr>
<tr>
<td>NTT-8</td>
<td>0</td>
<td>0.008</td>
<td>~2</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>515</td>
<td>245</td>
<td></td>
</tr>
<tr>
<td>NTT-11</td>
<td>0.02</td>
<td>~0.02</td>
<td>0.20</td>
<td>5.355</td>
<td>13.164</td>
<td>5.395</td>
<td>463</td>
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<td>~10</td>
</tr>
<tr>
<td>NTT-10</td>
<td>0.06</td>
<td>0.05</td>
<td>0.45</td>
<td>5.357</td>
<td>13.182</td>
<td>5.389</td>
<td>428</td>
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<td>~</td>
</tr>
<tr>
<td>IMS-1</td>
<td>0.08</td>
<td>~0.07</td>
<td>1.60</td>
<td>5.364</td>
<td>13.189</td>
<td>5.364</td>
<td>381</td>
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</tr>
<tr>
<td>NTT-30</td>
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<td>0.75</td>
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<td>~</td>
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<tr>
<td>NTT-35</td>
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<td>~</td>
<td>265</td>
<td>~</td>
<td>10</td>
</tr>
<tr>
<td>MIT-11</td>
<td>0.12</td>
<td>~0.06</td>
<td>0.60</td>
<td>5.353</td>
<td>13.204</td>
<td>5.353</td>
<td>245</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
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<td>5.355</td>
<td>13.221</td>
<td>5.355</td>
<td>224</td>
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<td>~</td>
</tr>
<tr>
<td>KOS-1</td>
<td>0.15</td>
<td>0.13</td>
<td>0.60</td>
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<td>~</td>
<td>~</td>
<td>200</td>
<td>~</td>
<td>33</td>
</tr>
</tbody>
</table>
Appendix C: Group Theory for the Tetragonal-Orthorhombic Transition

This appendix outlines some of the group theory analysis necessary to write down the Landau free energy for the tetragonal-orthorhombic transition. A more detailed description of the procedure may be found in Evans-Lutterodt.\(^1\)

The character tables for wavevectors at the \(\Gamma\) point, \(k^\prime = 0\), and the \(X\) point, \(k^\prime = (\frac{1}{2},\frac{1}{2},0)\), are given in tables C.1 and C.2. Note that the point group of the tetragonal phase is \(D_{4h}\), and the group of \(k^\prime\) at the \(X\) point is \(D_{2h} = D_2 \times i\). The notation for the irreducible representations is that of Tinkham.\(^2\)

**TABLE C.1. \(\Gamma\) Point Character Table of the Tetragonal Phase**

<table>
<thead>
<tr>
<th></th>
<th>(E)</th>
<th>(C_{2z})</th>
<th>(2C_{4z})</th>
<th>(C_{2x})</th>
<th>(C_{2y})</th>
<th>(C_{2xy})</th>
<th>(I)</th>
<th>(IC_{2z})</th>
<th>(2IC_{4z})</th>
<th>(IC_{2x})</th>
<th>(IC_{2y})</th>
<th>(IC_{2xy})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{1g})</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_{2g})</td>
<td>1</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
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<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
</tr>
<tr>
<td>(B_{1g})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>1</td>
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<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
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<td>(E_{g})</td>
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<td>0</td>
<td>0</td>
<td>2</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(A_{1u})</td>
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<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
</tr>
<tr>
<td>(A_{2u})</td>
<td>1</td>
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<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
</tr>
<tr>
<td>(B_{1u})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>1</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
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<td>(\bar{1})</td>
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<tr>
<td>(B_{2u})</td>
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<td>(\bar{1})</td>
<td>(\bar{1})</td>
<td>(\bar{1})</td>
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<td>(\bar{1})</td>
<td>(\bar{1})</td>
</tr>
<tr>
<td>(E_{u})</td>
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<td>0</td>
<td>0</td>
<td>(\bar{2})</td>
<td>(\bar{2})</td>
<td>0</td>
<td>0</td>
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<td>(\bar{2})</td>
<td>(\bar{2})</td>
<td>(\bar{2})</td>
</tr>
</tbody>
</table>

---

TABLE C.2. X Point Character Table of the Tetragonal Phase

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>C₂ₓ</th>
<th>C₂ₓᵧ</th>
<th>C₂ᵧ</th>
<th>l</th>
<th>IC₂ₓ</th>
<th>IC₂ₓᵧ</th>
<th>IC₂ᵧₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aᵣ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B₁ᵣ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B₂ᵣ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B₃ᵣ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Aᵣ  | 1   | 1   | 1    | 1    | 1   | 1    | 1     | 1     |
| B₁ᵣ | 1   | 1   | 1    | 1    | 1   | 1    | 1     | 1     |
| B₂ᵣ | 1   | 1   | 1    | 1    | 1   | 1    | 1     | 1     |
| B₃ᵣ | 1   | 1   | 1    | 1    | 1   | 1    | 1     | 1     |

In order to deduce the symmetry properties of the B₃ᵣ soft X point mode, it is convenient to work with a specific basis function for this irreducible representation. It is easy to show using projection operators that the following Bloch wavefunction has B₃ᵣ symmetry.

\[
\Phi_1 = e^{i\pi(x + y)} \left[ \sin\left(\frac{2\pi}{a}x\right) + \sin\left(\frac{2\pi}{a}y\right) \right] \sin\left(\frac{2\pi}{c}z\right) \tag{C-1}
\]

The star of the X point wave vector is \( k'_1 = (\frac{1}{2},\frac{1}{2},0)_T \) and \( k'_2 = (-\frac{1}{2},\frac{1}{2},0)_T \). \( \Phi_1 \) above has wavevector \( k'_1 \); the \( k'_2 \) partner function for \( \Phi_1 \) is

\[
\Phi_2 = e^{i\pi(-x + y)} \left[ \sin\left(\frac{2\pi}{a}y\right) - \sin\left(\frac{2\pi}{a}x\right) \right] \sin\left(\frac{2\pi}{c}z\right) \tag{C-2}
\]

Applying the symmetry elements of the D₄ᵣ point group to these functions yields the following transformation properties.
TABLE C.3. Transformation Properties of $\Phi_1$ and $\Phi_2$

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Transformation</th>
<th>Symmetry</th>
<th>Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
<td>$I$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
</tr>
<tr>
<td>$C_{2z}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
<td>$IC_{2z}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
</tr>
<tr>
<td>$C_{4z}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
<td>$IC_{4z}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
</tr>
<tr>
<td>$C_{4z}^{-1}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
<td>$IC_{4z}^{-1}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
</tr>
<tr>
<td>$C_{2x}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
<td>$IC_{2x}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
</tr>
<tr>
<td>$C_{2y}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
<td>$IC_{2y}$</td>
<td>$\Phi_1 \rightarrow \Phi_2$; $\Phi_2 \rightarrow \Phi_1$</td>
</tr>
<tr>
<td>$C_{2xy}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
<td>$IC_{2xy}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
</tr>
<tr>
<td>$C_{2xy}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
<td>$IC_{2xy}$</td>
<td>$\Phi_1 \rightarrow \Phi_1$; $\Phi_2 \rightarrow \Phi_2$</td>
</tr>
</tbody>
</table>

Given these transformation properties, it is easy to verify that the Landau free energy given in equation 5-2 is invariant under all symmetry elements of the $I4/mmm$ space group.

The symmetry of the orthorhombic strain field, $\eta$, may be deduced by considering the atomic displacements which produce this strain. As can be seen in figure C.1, the strain displacements are invariant under the following symmetry operations: $E$, $C_{2z}$, $C_{2xy}$, $C_{2xy}$, $I$, $IC_{2x}$, $IC_{2xy}$, $IC_{2xy}$

![Cu lattice diagram](image)

**Figure C.1.** Orthorhombic Strain Atomic Displacements
In order to find the irreducible representation of this strain, note that the character for the symmetry elements listed above must be 1, while the other characters must not be 1. By examining table C.1, one can see that only the $B_{2g}$ irreducible representation satisfies this criteria.

The lowest order combination of $\Phi_1$, $\Phi_2$, and $\eta$ which is invariant under all symmetry operations of the $I4/mmm$ space group will be deduced now. Note that both $\Phi_1$ and $\Phi_2$ must have even powers in an invariant expression, since the wave vector of $\eta$ is zero. Further, it is easy to show using projection operators that

$$\begin{align*}
\left[\Phi_1^2 - \Phi_2^2\right] &= \sin(2\pi x/a) \cdot \sin(2\pi y/a) \cdot \sin^2(2\pi z/a) - xyz^2 \\
\text{(C-3)}
\end{align*}$$

has $B_{2g}$ symmetry. Thus $\eta(\Phi_1^2 - \Phi_2^2) \sim x^2y^2z^4$, which is invariant under all symmetry operations of the $D_{4h}$ point group. This justifies equation 5-5.