Structural response to local charge order in underdoped but superconducting \( \text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4 \)

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We report an anomalous local structural response in the \( \text{CuO}_2 \) planes associated with the appearance of charge inhomogeneities at low temperature in underdoped but superconducting \( \text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4 \). We used pair distribution function analysis of neutron powder diffraction data. The increase in the Cu-O bond length distribution at low temperature has an onset temperature which correlates with observations of charge and spin freezing seen by other probes.

Two unusual phenomena are observed in the normal state in the underdoped cuprates: a pseudo-gap and magnetic densities of states, and the possibility that the charge density in the superconducting planes of these materials is inhomogeneously distributed, possibly in a striped morphology. It is important to establish the role that charge inhomogeneities have in the high-\( T_c \) phenomenon itself. Unlike the pseudo-gap phenomenon, their universal observation among different high-\( T_c \) systems has not been established. The strongest evidence for them in the cuprates is the observation of long range ordered static charge stripes in \( \text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4 \) compounds. These have been seen in both insulating and superconducting compounds but they appear to compete with the superconductivity. On the other hand fluctuating short range ordered charge stripes may play an active role in the high-\( T_c \) phenomenon. They also give a natural explanation for the observation of incommensurate spin fluctuations which have been seen in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) and \( \text{YBa}_2\text{Cu}_3\text{O}_{6+\delta} \) as well as being able to explain various other experimental observations. It is important to establish both the ubiquity of charge inhomogeneities in underdoped cuprates and their relationship to superconductivity. Here we present diffraction evidence that establishes the presence of temperature dependent atomic scale structural inhomogeneities at low temperature in underdoped but superconducting \( \text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4 \) samples. This observation is naturally explained by the appearance of charge inhomogeneities at low temperature in these samples. The inhomogeneities appear at a temperature which correlates with spin and charge freezing inferred from transport, NQR, and XANES measurements.

We used the atomic pair distribution function (PDF) analysis of neutron powder diffraction data to study the local structure of \( \text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4 \). Structural distortions coming from charge inhomogeneities appear in the PDF as an anomalous broadening of the nearest neighbor in-plane Cu-O bond length distribution. The average in-plane Cu-O bond length shortens on hole doping. This is observed experimentally and is expected on the grounds that holes are being doped into a \( \sigma^+ \) antibonding band thus stabilizing the bond. Charge inhomogeneities imply a coexistence of heavily and lightly doped regions of the \( \text{CuO}_2 \) plane. The lattice will respond if the charge inhomogeneities are fluctuating on phonon time-scales or slower. This will result in a distribution of lengths for the in-plane Cu-O bond and correspondingly to a broadening of the atomic pair distribution. This can be measured directly using the PDF analysis of neutron powder diffraction data. The PDF technique, which is common in the study of glasses, is equally well applied to crystalline systems where it reveals precise information about the local atomic structure going beyond the approximation of crystallinity.

Powdered samples of \( \text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4 \) \( (x = 0.125,0.15) \) of \( \sim 10 \text{ g} \) were synthesized using standard solid state techniques. The samples were characterized using x-ray diffraction and susceptibility measurements. The oxygen content was verified by measuring the \( c \)-axis parameter that was found to fall on the expected curve for stoichiometric samples. Neutron powder diffraction measurements were carried out on the High Intensity Powder Diffractometer at the Manuel Lujan Neutron Scattering Center (MLNSC) at Los Alamos National Laboratory and on the Glasses, Liquids and Amorphous Diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The samples were sealed in vanadium tubes with He exchange gas. Data were collected as a function of temperature from room temperature down to 10 K using a closed cycle He refrigerator. Standard corrections were made to the raw data, to account for experimental effects such as sample absorption and multiple scattering, using the program PDFgetN, to obtain the total scattering structure function, \( S(Q) \). This contains both Bragg and diffuse scattering and therefore information about atomic correlations on all length scales. The PDF, \( G(r) \), is obtained by a Fourier transformation ac-
The resulting PDF, $G(r)$ (open circles). The solid line is a fit to the data of the crystallographic model with the difference curve below. Arrows indicate the PDF peaks at $Q_{\text{max}} = 7\text{ Å}^{-1}$ for $r = 1\text{ Å}$ and $r = 7.2\text{ Å}$ whose widths are plotted in Fig. 2.

According to $G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin qr dQ$, where $Q$ is the magnitude of the scattering vector. The PDF gives the probability of finding an atom at a distance $r$ away from another atom. The PDF from $La_{1.875}Sr_{0.125}CuO_4$ at 300 K is shown in Fig. 1(b) with the diffraction data in the form of $Q[S(Q) - 1]$ in Fig. 1(a). Superimposed on the PDF is a fit to the data of the average structure model using the profile fitting least-squares regression program, PDFFIT [33]. The $S(Q)$ data were terminated at $Q_{\text{max}} = 23\text{ Å}^{-1}$. This is a conservative value for $Q_{\text{max}}$ in typical PDF measurements. The data from high-$Q$ has a poorer signal-to-noise ratio because of the effect of the Debye-Waller factor. By eliminating it from the Fourier transform we improve the signal-to-noise ratio of our data and the temperature to temperature reproducibility of the PDFs. This reduces the possibility that observed effects are noise artifacts. We can therefore have confidence that any effects that survive this conservative approach to Fourier transforming the data are real.

In $La_{2-x}(Sr,Ba)_xCuO_4$, the first peak in the PDF at $r = 1.9\text{ Å}$ originates from the in-plane Cu-O bond. The width of this peak comes from the relative motion of nearest neighbor in-plane Cu-O pairs, plus any static or quasistatic bond-length distribution, averaged over the whole sample. We have studied the mean square width, $\sigma^2 \propto \langle u^2 \rangle$, of this peak as a function of temperature for a series of underdoped $La_{2-x}(Sr,Ba)_xCuO_4$. The results are reproduced in Fig. 2. Peak profiles in the PDF are well modelled using a Gaussian function convoluted with a Sinc function, $\sin Q_{\text{max}} r/ Q_{\text{max}} r$ [33]. The Sinc function results from Fourier transforming the finite-range data. Since $Q_{\text{max}}$ is a known experimental parameter it is possible to extract intrinsic peak widths for the underlying Gaussian distributions. The results of this convoluted fitting process are shown in Fig. 2(a)-(c). It is clear from the Figure that the peak width decreases with decreasing temperature as expected. However, below a certain temperature the Cu-O bond length distribution broadens on further decrease of temperature. This effect cannot be explained by normal thermal behavior as indicated by the solid lines which have the expected Einstein form [34]. There are also no structural phase transitions occuring at these temperatures.

The same qualitative result was obtained from the data directly without carrying out a convoluted fit. First, we simply plot the inverse-squared PDF peak height, $1/h^2$, obtained directly from the data. This is a model independent measure of $\sigma^2$ since the integrated area under
the PDF peaks is conserved. The inverse-squared peak heights are shown in the insets to Fig. 2(a)-(c). We also fitted the 1.9 Å PDF peak with pure Gaussian functions that were not convoluted with Sinc functions (not shown). Both these approaches reproduced the qualitative result shown in Fig. 2(a)-(c) giving us confidence that it has a real origin and is not an artifact of the convoluted fitting procedure. All of these measures of the PDF peak width confirm the observation in the convoluted peak fits that the underlying in-plane Cu-O pair distribution is getting broader with decreasing temperature below some temperature, $T_{si}$.

Peaks not involving in-plane Cu-O pairs, at higher values of $r$, in the PDF behave canonically. This is shown in Fig. 2(d) where $1/h^2(T)$ of the peak at $r = 7.2$ Å (indicated with an arrow in Fig. 2) from each of the samples is plotted with an Einstein curve superimposed. As expected, no upturn is observed at low temperature.

The broadening of the $r = 1.9$ Å PDF peak at low temperature can be explained if charge inhomogeneities, such as charge stripes, are manifesting themselves in the structure at low temperature. This will occur both if the electronic correlations are appearing at low temperature or if preexisting correlations are slowing down and beginning to interact with the lattice. It was shown in an earlier PDF study that a gradual broadening with increasing doping at 10 K of the $r = 1.9$ Å PDF peak in La$_{2-x}$Sr$_x$CuO$_4$ could be well explained as a microscopic coexistence of heavily doped and undoped regions of the copper-oxygen plane. The $x$-dependence of this PDF peak width measured at 10 K is reproduced in the inset to Fig. 2(d). This can be compared with the intrinsic peak widths at low temperature from this study.

The original $x$-dependent data were interpreted as follows. The relatively sharp peaks in the $x = 0$, 0.25, and 0.30 data were assumed to have a single valued bond length broadened by thermal and zero point motion resulting in a mean-square width of $\sim 30$ pm$^2$. The relatively broader peaks observed in the underdoped compounds ($x = 0.05$, 0.10, 0.125, 0.15) could be explained as a superposition of sharp peaks that are shifted in position originating, respectively, from less doped and more heavily doped regions of the copper oxide plane. This very simple model independent analysis is likely to be an oversimplification of the real situation where local strains may lead to broader distributions of the PDF peaks; however, it establishes unequivocally that the observed effects in the PDF are consistent with structural distortions originating from charge inhomogeneities. Despite the current measurements being made on different materials at different times using different diffractometers it is clear that both the low-temperature thermal width of 25-31 pm$^2$ extrapolated from the Einstein model, as well as the excess peak height of $\sim 10 - 15$ pm$^2$, are in rather good agreement with our earlier observation of the $x$-dependence of La$_{2-x}$Sr$_x$CuO$_4$. This indicates that the underlying origin of the peak broadening is the same.

The in-plane Cu-O pair correlation has been studied in a number of XAFS measurements. The data of Lanzara et al. qualitatively suggest an upturn in the width of the distribution at low temperature. However, this result may not be significant since later work suggests that uncertainties in unpolarized XAFS measurements are larger than the observed effects and that polarized XAFS measurements are necessary to obtain higher precision. In particular, this latter study puts an upper limit of 0.017 Å on possible nonthermal disorder amplitude present in the in-plane Cu-O bond distribution of La$_{1.875}$Ba$_{0.125}$CuO$_4$. This is not far from our suggestion of a $\sim 0.02$ Å splitting observed in La$_{2-x}$Sr$_x$CuO$_4$ and in the current work. Our data will be compared with the result of Haskel et al. in more detail elsewhere.

We have extracted a temperature, $T_{si}$, where the structural inhomogeneities set in by taking the difference, $\Delta \sigma^2$, between the observed width and the Einstein curves plotted in Fig. 2. The resulting values for $T_{si}$ are 125 K for La$_{1.875}$Sr$_{0.125}$CuO$_4$ and 60 K and 100 K for La$_{1.85}$Sr$_{0.15}$CuO$_4$ and La$_{1.85}$Ba$_{0.15}$CuO$_4$, respectively. These are shown in Fig. 2 as solid hexagons. The estimated error bars are rather large since the exact value of $T_{si}$ depends on parameters used in the Einstein fits; also our data-sets are somewhat sparse. However, they give a temperature scale where the effects of charge inhomogeneities first appear in the local structure.

In Figure 2 we show a phase diagram for La$_{2-x}$Sr$_x$CuO$_4$ with $T_{si}$ plotted along with $T_c$ and $T^*$ obtained from the literature. Superimposed on this diagram is $T_{sf}$, the onset temperature for NQR signal “wipe-out”, $T_u$, the temperature where the deviation of the normalized resistivity, $\rho/\rho(0)$, reaches a critical value, and $T_x$, the temperature where an anomaly is seen in XANES data. All of these characteristic temperatures have been associated with charge or spin freezing. It is clear that the $T_{si}$'s obtained from the present data correlate quite well with the other measures of spin and charge freezing.

Our results clearly show that the charge inhomogeneities are strongly coupled to the lattice in La$_{2-x}$(Sr,Ba)$_x$CuO$_4$ compounds and become pinned by the lattice at low temperature. In the absence of Nd the pinning is not complete and the charges do not order over long range, even at $x=0.125$ in the Sr doped compound. Nonetheless, their strong coupling to the lattice will make them quite immobile. Our measurements yield the instantaneous structure and we cannot distinguish whether the inhomogeneities are static or fluctuating phonon time scales or slower. It will be interesting to see whether similar effects are seen in the PDF of HgBa$_2$CuO$_{4+\delta}$ which is a single layer cuprate superconductor like the La$_{2-x}$(Sr,Ba)$_x$CuO$_4$ compounds but has a much higher $T_c$. It is possible that electronically driven
stripes are important for superconductivity but a strong coupling to the lattice is destructive. However, phonon anomalies have been associated with charge stripe formation in YBa$_2$Cu$_3$O$_{6.5}$ and theories exist in which the charge stripes are stabilized by the lattice. Resolving this issue will be a key component in gaining a complete understanding of high temperature superconductivity.

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FIG. 3. Phase diagram of La$_{2-x}$Sr$_x$CuO$_4$ showing the temperatures of pseudogap opening, $T^*$ [1], XANES anomaly, $T_x$ [2], NQR spin freezing, $T_{sf}$ [3], transport upturn, $T_u$ [4] and the $T_u$'s determined from the present measurements. $T_{si}$ is known to be below 10 K for La$_{2-x}$Sr$_x$CuO$_4$ with $x > 0.2$ [2] as indicated. $T_c$ is shown as solid circles joined by a line. The inset is the same phase diagram on an expanded temperature scale.

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