

Neutron Diffraction Evidence of Microscopic Charge Inhomogeneities in the CuO_2 Plane of Superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 \leq x \leq 0.30$)

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High-resolution atomic pair distribution functions have been obtained using neutron powder diffraction data from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ over the range of doping $0 \leq x \leq 0.30$ at 10 K. Despite the average structure getting less orthorhombic, we see a *broadening* of the in-plane Cu-O bond distribution as a function of doping up to optimal doping. Thereafter the peak abruptly sharpens. The peak broadening can be well explained by a local microscopic coexistence of doped and undoped material. This suggests a crossover from a charge inhomogeneous state at and below optimal doping to a homogeneous charge state above optimal doping.

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There is mounting interest in the possibility that the charge distribution in the CuO_2 planes of the high-temperature superconductors (HTS) is microscopically inhomogeneous [1,2] and that this has a bearing on the high-temperature superconductivity itself. An inhomogeneous charge distribution has been predicted theoretically [3–7]. There is also mounting experimental evidence that microscopic charge inhomogeneities exist in particular cuprate samples. The most compelling evidence for this comes from the observation from neutron diffraction of stripes of localized charge in $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ [2,8]. However, such direct evidence for charge stripes has been seen only in insulating compounds or in samples where this ordering competes with superconductivity [9]. The evidence supporting the presence of dynamic local charge stripe distributions in the bulk of *superconducting* samples is based primarily on the observation of incommensurate spin fluctuations [10–13]. We present local structural evidence that supports the fact that the charges are inhomogeneous in the underdoped and optimally doped region of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ phase diagram, consistent with the presence of charge domains or dynamic charge stripes. The charge distribution becomes homogeneous on crossing into the overdoped region. The clear observation of these effects in the local structure also underscores the point that there is a strong electron-lattice coupling, at least to particular distortion modes, in these materials. We note that the disappearance of the structural distortions, and therefore the charge inhomogeneities, correlates with the disappearance of the normal-state pseudogap [14] in these materials.

The presence of charge inhomogeneities in the CuO_2 planes implies profound consequences for the local structure. It is well known that the average Cu-O bond length changes as the charge state of copper changes. Thus, the Cu-O bond in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shortens from 1.904 to 1.882 Å as x changes from 0 to 0.2 [15] and the aver-

age copper charge changes from 2+ to $\sim 2.2+$. This is a generic feature of variably dopable HTS samples and comes about because the Cu-O bond is a covalent antibonding state which is stabilized by removing electron density from it. Clearly, if the doped charge in the CuO_2 planes is inhomogeneously distributed, such that some copper sites have more charge than others, a distribution of in-plane Cu-O bond lengths will exist. A high resolution measurement of the in-plane Cu-O bond length *distribution* as a function of doping will therefore reveal the extent of charge inhomogeneities.

We have used the atomic pair distribution function (PDF) analysis of neutron powder diffraction data to measure accurate Cu-O bond length distributions with high resolution for a series of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples with ($0 \leq x \leq 0.3$). The ability of high-resolution PDF studies to reveal local bond-length inhomogeneities which are not apparent in the average structure has been clearly demonstrated [16]. The samples studied cover the range from undoped, through underdoped and optimally doped ($x = 0.15$), to the overdoped regime. We find that at 10 K the mean-square width of the bond-length distribution, σ^2 , increases approximately linearly with x until optimal doping above which it sharply decreases and returns to the value of the undoped material by $x = 0.25$. This is strong evidence for charge inhomogeneities in the underdoped and optimally doped regimes as we discuss below. This increase in bond-length distribution can be well explained by a linear superposition of the local structures of undoped and heavily doped material.

Samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.0, 0.05, 0.1, 0.125, 0.15, 0.2, 0.25,$ and 0.3 were made using standard solid state synthesis. Mixtures of $\text{La}_2\text{O}_3, \text{SrCO}_3,$ and CuO were reacted at temperatures between 900 and 1050 °C with intermediate grindings, followed by an annealing step in air at 1100 °C for 100 h and in oxygen at 800 °C for 100 h. The long anneals were carried out to ensure

doping homogeneity in the samples. The lattice c -axis parameter is a sensitive measure of oxygen stoichiometry [12]. Its value was determined for each of our samples through Rietveld refinement of the data. It varies smoothly with x as expected for stoichiometric samples and lies on the c axis vs x curve of Radaelli *et al.* [15] within the scatter of their data. Neutron powder diffraction data were collected at 10 K on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Approximately 10 g of finely powdered sample was sealed in a cylindrical vanadium tube with He exchange gas. The samples were cooled using a closed-cycle He refrigerator. The data were corrected [17] for experimental effects and normalized to obtain the total structure function $S(Q)$, where Q represents neutron momentum transfer. The PDF, $G(r)$, is obtained by a Fourier transform of the data according to $G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin Qr dQ$. PDFs from these samples are shown in Figs. 5–8 of Ref. [18] and in Fig. 3 of this paper. The PDFs examined in this paper used data over a range $0.7 < Q < 28 \text{ \AA}^{-1}$.

We are interested in extracting the width of the distribution of in-plane Cu-O bond lengths. This information is contained in the width of the first PDF peak at $\sim 1.9 \text{ \AA}$. The peak width comes from the thermal and zero-point motion of the atoms plus any bond-length distribution originating from other effects such as charge inhomogeneities. We can determine the latter by considering the PDF peak width of this peak as a function of doping at 10 K. Three independent measures of the peak width all show that the width increases significantly with doping up to $x = 0.15$, beyond which the peak quickly sharpens. First, this behavior is evident by simply looking at the data shown in Fig. 1. This shows the low- r region of the PDF around the $r = 1.9 \text{ \AA}$ peak as a function of x . Since we want to compare the relative peak widths (and heights), in this figure the peaks have been shifted to line up the peak centroids and rescaled slightly to ensure that the integrated intensity of each peak is the same. It is clear that some of the peaks are significantly broader than others with lower peak heights and less steeply sloping sides. We have quantified this by fitting the peak with a single Gaussian. The Gaussian is first convoluted with the Fourier transform of the step function which was used to terminate the data [19]. This accounts for any termination ripples in the data introduced by the Fourier transform of the finite range data set and does not introduce any additional parameters into the fit. The fitting parameters were peak position, scale factor, and width. The baseline is set by the average number density of the material and this was fixed at $\rho_0 = 0.07299 \text{ \AA}^{-3}$. The results are shown in Fig. 2 as the solid circles. The mean-square width of the distribution increases monotonically (and almost linearly) with x until $x = 0.15$. Between 0.15 and 0.2 the peak abruptly sharpens and returns to the width of the undoped sample by $x = 0.25$. The same behavior can be obtained from the data in a totally model-

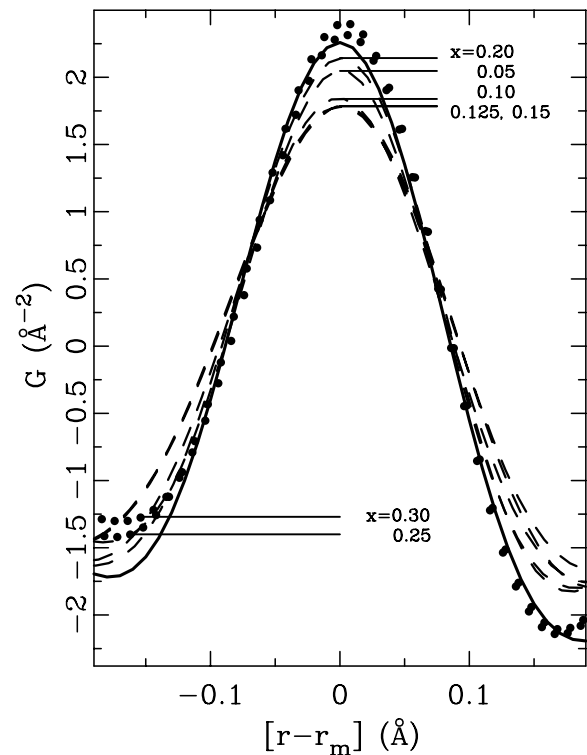


FIG. 1. PDF peak coming from the in-plane Cu-O bond for various doping levels (solid line: undoped case; solid circles: overdoped cases; dashed lines: intermediate doping cases). The peaks have been shifted so that their centers line up at $r_m = 1.91 \text{ \AA}$.

independent way. If the integrated area of a Gaussian is constant, the height is inversely proportional to the width. Thus, the peak height, h , of the rescaled data shown in Fig. 1 should be inversely proportional to the width. The open squares in Fig. 2 show C/h^2 , where h was determined directly from the peak maximum in the data and the constant C was chosen to make the $x = 0.0$ points line up. There is excellent agreement lending confidence to the results from the fitting.

We would like to discuss possible origins for these doping dependent changes in Cu-O bond-length distribution. First, we rule out the possibility that it simply comes from changes in the orthorhombicity of the sample. The Cu-O PDF peak first broadens smoothly with increasing doping then dramatically sharpens at a composition close to the low-temperature orthorhombic (LTO) to high-temperature tetragonal (HTT) structural phase boundary. This behavior does not reflect the monotonic decrease in orthorhombicity of the average structure. Indeed, in the overdoped region the PDF peak returns to the same narrow width it had in the undoped material which has the largest orthorhombic distortion of any of the samples. We also note that the in-plane Cu-O bonds are not expected to be sensitive to the orthorhombic distortion. They lie along the unit cell diagonals and not along the unit cell edges in the orthorhombic unit cell. In this case an orthorhombic distortion will

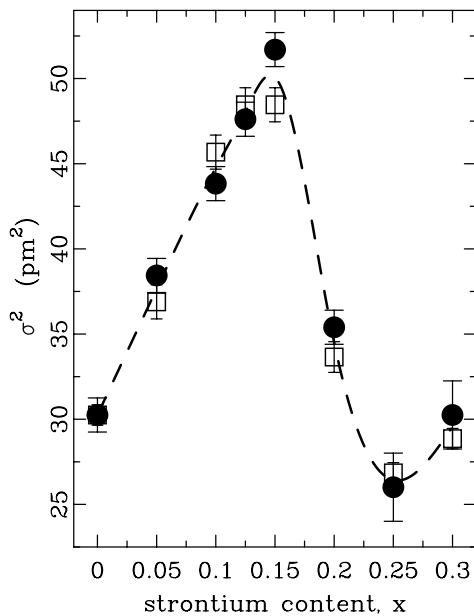


FIG. 2. Peak width of the in-plane Cu-O PDF peak as a function of doping obtained by fitting a Gaussian (solid circles). The data are plotted as σ^2 , where σ is the Gaussian standard deviation. The inverse peak-height squared of the peaks in Fig. 1 scaled so the $x = 0.0$ points line up is shown as open squares. The dashed line is a guide for the eye.

change the bond length but will not lead to two distinct bond lengths.

Next we show that the observed behavior cannot be explained by doping dependent changes in the octahedral tilts. The average [15] (and local) [18] tilt amplitude monotonically decreases with increasing doping which does not correlate with the behavior of the Cu-O bond length distribution. On the other hand, PDF peaks at higher- r do sharpen monotonically with increasing x reflecting the reduced octahedral tilt amplitude [18]. We also rule out the idea that the observed Cu-O peak broadening is an effect of size-effect disorder due to doping since the peak sharpens dramatically above $x = 0.2$ where the dopant induced disorder should be the greatest. We also note that size-effect dopant induced disorder is expected to have a large effect on octahedral tilts and a small effect on Cu-O bond lengths since the energy to change a Cu-O-Cu bond angle is much less than the energy to stretch the short Cu-O covalent bond. Furthermore, the extent of dopant induced tilt disorder is relatively small in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as evidenced by the observation that higher- r PDF peaks sharpen on increased doping in this material. These peaks sharpen because of a decrease in both the average orthorhombicity and octahedral tilt angle with increased doping. However, significant size-effect octahedral tilt disorder due to the chemical dopants tends to counter this effect, as seen in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [20,21]. We can also rule out structural fluctuations associated with the HTT-LTO transition. First, these fluctuations will affect primarily octahedral tilts and local orthorhombicity (the two order parameters

of this structural transition) and, as we have discussed, the Cu-O bond is expected to be quite insensitive to disorder in these parameters. However, in addition, we would expect these fluctuations to be largest when the structural phase transition temperature, T_s , is closest to our measurement temperature. These temperatures are closest for the $x = 0.2$ sample ($T_s = 60$ K [22], $T_{\text{meas}} = 10$ K) and this sample exhibits a narrow distribution of Cu-O bond lengths. The largest distribution of Cu-O bond lengths is seen for $x = 0.15$ where $T_s = 180$ K.

The observed behavior of the Cu-O bond-length distribution is best explained by the presence of charge inhomogeneities. As we have described, the charge state of copper has a direct effect on the Cu-O bond length with the bond length decreasing with increasing doping. Charge inhomogeneities will, thus, give rise to a distribution of Cu-O bond lengths. Increased doping will result in more Cu-O bonds being affected and therefore a larger measured effect in the PDF, as observed. Above optimal doping the PDF peak width abruptly sharpens to its value in the undoped material. This is consistent with the idea that, in the overdoped region, the charge distribution in the Cu-O planes is becoming homogeneous.

We now discuss independent evidence from the data which supports this picture. In Fig. 3(a) we show the low- r region of the PDF from the $x = 0.0$ and $x = 0.25$ samples. Referring to Fig. 2, we see that these two data sets have relatively *narrow* Cu-O bond-length distributions. Furthermore, in Fig. 3(a) it is apparent that the peak position has shifted due to the change in the average Cu-O bond length with doping, as expected. The difference curve below the data shows that the two data sets are quite different due to the significant structural differences. In Fig. 3(b) we show the intermediate $x = 0.1$ data set plotted as open circles. This peak is centered at a position shown by the dashed line which is intermediate between the positions of the $x = 0.0$ and $x = 0.25$ data sets. Referring to Fig. 2 we see that the Cu-O bond-length distribution is relatively *broad* at this composition. Plotted on top of the $x = 0.1$ data set in Fig. 3(b) as the solid line is the PDF obtained by taking a linear combination of the $x = 0.0$ and $x = 0.25$ data sets in the 1:1 ratio, without rescaling the data at all. The difference curve is shown below. The good agreement clearly demonstrates that the observed PDF peak position *and* broadening of the $x = 0.1$ data set is entirely *consistent* with there being an underlying bimodal bond-length distribution consistent with heavily doped and undoped regions of the CuO_2 plane. We can infer from this analysis that the difference in the bond lengths is ~ 0.024 Å which is the difference between the average bond lengths of the $x = 0.0$ and $x = 0.25$ samples.

Finally, we note that the PDFs from underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are consistent with the presence of CuO_6 octahedral tilt disorder in the samples. In an earlier paper [18] we showed that the measured PDFs could be well explained by a local structure which contains a mixture

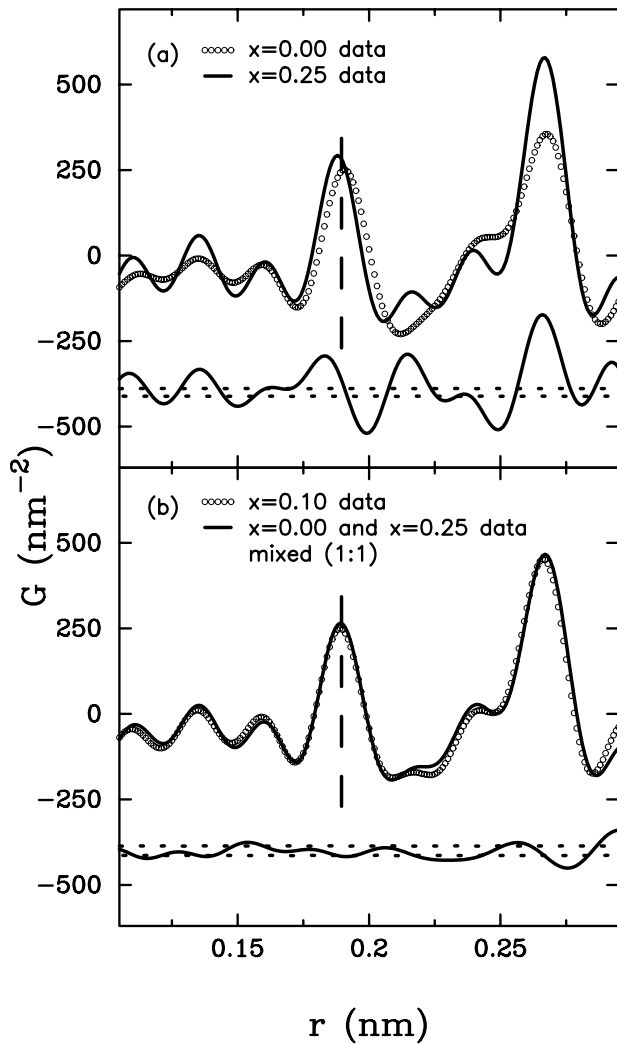


FIG. 3. (a) PDFs from the 10 K data from the $x = 0.0$ (open circles) and $x = 0.25$ (solid line) samples. The difference is plotted below. The dashed lines indicate expected uncertainties due to random errors. (b) PDF from $x = 0.1$ data at 10 K (open circles). The solid line shows the PDF obtained by making a linear combination in a (1:1) ratio of the PDFs shown in (a). See the text for details.

of large and small octahedral tilts. We note here that we also have evidence from the PDFs for the presence of tilt-directional disorder in the sense that there is a mixture of $\langle 100 \rangle$ (LTO) and $\langle 110 \rangle$ (low-temperature tetragonal or LTT) symmetry tilts present in the local structure. This will be reported in detail elsewhere [21].

In summary, we have presented evidence from neutron diffraction data which strongly supports the idea that

doped charge in the CuO_2 planes of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for $0 < x \leq 0.15$ and at 10 K is inhomogeneous. For doping levels of $x = 0.2$ and above the charge distribution in the Cu-O plane becomes homogeneous. This presumably reflects a crossover towards more Fermi-liquid-like behavior in the overdoped regime.

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