Neutron scattering study of the effects of dopant disorder on the superconductivity and magnetic order in stage-4 La$_2$CuO$_{4+y}$

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We report neutron scattering measurements of the structure and magnetism of stage-4 La$_2$CuO$_{4+y}$ with $T_c \simeq 42$ K. Our diffraction results on a single crystal sample demonstrate that the excess oxygen dopants form a three-dimensional ordered superlattice within the interstitial regions of the crystal. The oxygen superlattice becomes disordered above $T \simeq 330$ K, and a fast rate of cooling can freeze-in the disordered-oxygen state. Hence, by controlling the cooling rate, the degree of dopant disorder in our La$_2$CuO$_{4+y}$ crystal can be varied. We find that a higher degree of quenched disorder reduces $T_c$ by $\sim 5$ K relative to the ordered-oxygen state. At the same time, the quenched disorder enhances the spin density wave order in a manner analogous to the effects of an applied magnetic field.

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One of the central topics of research on highly correlated electron systems is the interplay between the competing phases which exist at low temperatures. Often, small changes in the microscopic parameters lead to drastic changes in the macroscopic properties. In the field of high-$T_c$ superconductivity, there has been much recent discussion about the different types of order that may compete with the superconducting state. Examples of these possible orders include: antiferromagnetism, spin-stripes, charge-stripes, $d$-density wave order, staggered flux phases, and circulating-current phases, among others. This discussion has been very productive because many of the proposed theories have predictions which can be directly tested by experiments, often with scattering techniques. For example, in the La$_2$CuO$_4$ family of materials, neutron scattering experiments have revealed that spin-density wave (SDW) order competes with the superconductivity.\cite{2, 3, 4, 5, 6} Recent work investigating the effects of applied magnetic fields indicates that these two order parameters coexist at the microscopic level even though they are repulsively coupled.\cite{3, 4, 6, 7} There is increasing evidence which suggests that stripe phases (static or dynamic) exist in several of the cuprate superconductors, including YBa$_2$Cu$_3$O$_{6+x}$\cite{8, 9} and Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$\cite{10, 11}.

In order to make further progress, it is important to determine whether the experimentally observed order parameters are intrinsic to the CuO$_2$ plane, or whether they arise due to subtle aspects of the materials' crystal structure or degree of disorder. Recent work on YBa$_2$Cu$_3$O$_{6+x}$\cite{8, 9} has highlighted the importance of oxygen ordering within the chain layers in producing optimal superconducting properties and robust magnetism.\cite{2, 12} We have studied the effects of dopant disorder on the superconductivity and SDW order in the single-layer copper-oxide superconductor La$_2$CuO$_{4+y}$. The excess oxygen dopants fill interstitial regions of the lattice and are mobile at high temperatures. We find that the oxygen dopants form an ordered lattice at low temperature, and we have developed a method to control the degree of dopant disorder. Hence, we can investigate the role of disorder in the phase diagram of this cuprate superconductor, and we have applied this new tool to probe the relationship between the competing phase of the cuprates.

Our earlier studies have shown that the oxygen doped La$_2$CuO$_{4+y}$ material has a staged structure, which differentiates it from the related La$_{2-x}$Sr$_x$CuO$_4$ material.\cite{13} The evidence for staging behavior comes from a modulation of the octahedral tilt pattern along the c-axis. This results in superlattice diffraction peaks displaced by a wavevector (0,0,$\Delta$) from the $Bmab$ superlattice positions. If the modulation has a period of $n$ unit cells, then the $L$-component of the wavevector has magnitude $\Delta = 1/n$ (and the structure is called stage-$n$). We note, however, these peaks only provide information regarding the octahedral tilt arrangement and, thus, are only indirect evidence that the distribution of oxygen dopants is modulated. In principle, the excess oxygens themselves also contribute to the total scattering cross section. Hence, we have searched for superlattice peaks which would be associated with a 3D lattice of ordered oxygen dopants in a stage-4 crystal of La$_2$CuO$_{4+y}$.

Our experiments were carried out on a floating-zone grown crystal which was electrochemically oxidized to produce superconducting La$_2$CuO$_{4+y}$ with $y \simeq 0.12$ and $T_c \simeq 42$ K. (The sample in this paper is the same as “Sample 1” in the work by Khaykovich et.al.\cite{3}) Elastic neutron scattering measurements were performed using the SPINS spectrometer at the NIST Center for Neutron Research in Gaithersburg, MD. Cold neutrons with incident energy of 5 meV were selected with a pyrolytic graphite monochromator, and collimation sequence of
32 – 40 – sample – 20 – blank was chosen. A cryogenically cooled Be filter was used to remove higher energy contamination from the neutron beam.

For the structural studies, the sample is initially mounted in the \((0KL)\) scattering zone. At low temperatures, we find peaks displaced from the fundamental nuclear Bragg positions by \((\pm \Delta_H, \pm \Delta_K, \pm \Delta_L)\). For example, near the \((0,0,6)\) nuclear Bragg peak, a weak superlattice peak is observed at \((0.09, 0.24, 5.5)\) at \(T = 9\) K as shown in Figure 1(A). Here, the \(H\)-direction is along the wide vertical resolution direction, and the value for \(\Delta_H\) is deduced to be \(0.09(2) a^*\) via scans of the spectrometer \(\chi\) angle. The components of the modulation wavevector in the scattering zone are \(\Delta_K = 0.24(1) b^*\) and \(\Delta_L = 0.50(2) c^*\). Eight peaks are observed near the \((0, 0, 6)\) Bragg position at \((\pm 0.09, \pm 0.24, 6 \pm 0.50)\) with approximately equal intensities. We have found similar peaks in a stage-6 sample, with the only difference being that \(\Delta_L \simeq \frac{1}{4}\). We note that Radaelli et al. \[14\] had previously observed similar peaks at slightly different locations in a sample which had a similar doping level as our stage-6 sample.

Since these new peaks are characterized by a wave vector displaced from the fundamental Bragg positions, this implies a new periodicity imposed on the simple repetition of the orthorhombic unit cell. A natural explanation for these peaks is that they originate from scattering from the interstitial oxygens themselves, which order into a 3D superstructure spanning many \(La_2CuO_4\) unit cells. The \(\Delta_L = 0.50(1)\) component of the modulation wave vector, within error, equals \(2/n\) where \(n = 4.0\) is the staging number for this crystal. Thus, the ordered oxygen lattice has \(1/2\) of the periodicity of the tilt modulation. This is exactly what is expected for our staging model\[13\] where there are two dominant layers of oxygen interstitials per staging unit cell. We have confirmed that similar superlattice peaks exist near other fundamental positions including \((2,0,0)\), \((0,2,0)\), and \((0,0,2)\). In addition, a weak peak is observed with double the modulation wavevector at \((2 \Delta_H, 2 + 2 \Delta_K, 2 \Delta_L)\) which corresponds to the second higher harmonic position. No intensity is observed at positions corresponding to stage-2 oxygen ordered peaks at \((\pm \Delta_H, \pm \Delta_K, 1)\). Due to the limited number of observed superlattice peaks, a complete structural model cannot be refined.

If the peak depicted by the open symbols in Fig. 1(A) is indeed attributable to an ordered lattice of oxygen dopants, then it should be possible to probe directly the effects of disordering the lattice thermally by heating the sample to elevated temperatures. Neutron diffraction measurements have been carried out at higher temperatures to identify the temperature above which the ordered lattice of interstitial oxygens melts. As shown in the figure, the diffraction peaks disappear when the temperature is increased above 330 K. The inset of the figure shows the temperature dependence. If the sample is cooled from 350 K to 9 K in less than 2 hours, the intensity of the peak does not recover. Hence, we have thermally disordered the oxygen lattice and quenched-in the disorder. The time scale for the excess oxygens to reorder is on the order of a few days at 300 K; we have confirmed that the oxygen order peaks are recovered after annealing the sample for one week at room temperature.

Figure 1(B) depicts scans through the staging superlattice peaks along the \(L\)-direction through the \(Bmab\) position. The filled circle data points are taken at \(T = 9\) K in the state with the ordered oxygen lattice. The large peaks symmetrically displaced by \(\Delta_L = \pm \frac{1}{4}\) from the center position of the scan indicate that the sample is predominately stage-4. The peaks displaced by \(\Delta_L = \pm \frac{1}{2}\) might appear to result from a stage-2 component. However, these peaks most likely result from scattering from the distortions of the octahedra near the dominant layers of the oxygen intercalants. When the crystal is cooled from 350 K to 9 K in less than 2 hours, the intensity of the peak does not recover. Hence, we have thermally disordered the oxygen lattice and quenched-in the disorder. The time scale for the excess oxygens to reorder is on the order of a few days at 300 K; we have confirmed that the oxygen order peaks are recovered after annealing the sample for one week at room temperature.
quenched from above 330 K (producing the disordered-oxygen state) these peaks lose more than 50% of their intensity, depicted by the open circle data points. On the other hand, the stage-4 peaks gain additional integrated intensity. We note that in measurements on a different stage-4 crystal, the peaks at $\Delta L = \pm \frac{1}{2}$ disappear entirely when the oxygens are disordered. This implies that these samples are, in fact, pure stage-4 and that higher order peaks previously interpreted as arising from stage-2 material reflect the ordered oxygen superlattice in a stage-4 structure.

This brings us to the question of the interplay between the oxygen ordering and the superconductivity. A different piece of a stage-4 sample with $T_c \approx 42$ K was placed in a SQUID magnetometer and put through a heating process similar to that described for the neutron scattering measurements. In each cycle, the sample was slowly heated to the target temperature, annealed at the target temperature for one hour, and then zero field cooled to 5 K. The low temperature shielding signal was then measured in an applied field of 50 G. The results are shown in Fig.2. The sample was not removed from the SQUID between cycles. Weighing the sample before and after the combined SQUID measurements confirmed the absence of any weight loss. There is a distinct change in the superconducting transition temperature between the 320 K anneal and the 330 K anneal. For the measured curves, $T_c^{\text{midpoint}}$ decreases from 37.8(2) K before the annealing cycles to 32.8(2) K after the annealing cycles, with the most rapid decrease occurring between annealing temperatures of 320 K and 330 K. The annealing temperature range which affects $T_c$ exactly matches the temperature at which the order-disorder transition occurs for the oxygen lattice. This clearly demonstrates that the ordering of the oxygen intercalant lattice in La$_2$CuO$_{4+y}$ is responsible for its optimal $T_c$.

In order to probe the effects of dopant disorder on the SDW, we performed magnetic neutron diffraction measurements before and after disordering the oxygen lattice. First, the SDW peaks were measured in the state with ordered oxygen dopants with the crystal mounted in the (HK0) zone. The results are depicted by the open circle data points in Fig. 3. Next, the sample was mounted in the (0KL) zone in order to monitor the destruction of the ordered oxygen lattice as described previously. The sample was then remounted in the (HK0) zone and quenched to 10 K within 4 hours of disordering the oxygens. The SDW peaks were measured again, with the oxygen dopants now in the disordered state. The configuration of the spectrometer was not altered between measurements of the SDW peaks (ie, the collimations, spectrometer alignment, and shielding were untouched). Hence the intensities of the SDW peaks before and after disordering the oxygen lattice may be directly compared with each other. As a check, we confirmed that the (200) nuclear Bragg peaks had the same intensity (within 2%) before and after annealing at 350 K. On the other hand, the intensity of the SDW peaks was significantly increased as shown by the filled circle data points in Fig. 3. Hence, we find that increasing the degree of dopant disorder increases the SDW order parameter. However, the positions and widths of the peaks remain the same.

The temperature dependence of the SDW order parameter in both the ordered-oxygen state and the disordered-oxygen state is shown in Fig. 4(A). The primary effect
The degree of dopant disorder reduces the intensity of the SDW peaks. The onset temperature for the SDW order does not change within the errors, remaining at \( T_M \sim 42 \text{ K} \). For comparison, we plot the temperature dependence of the SDW in an applied magnetic field of 7.5 T in Fig. 4(B). The data have been normalized to allow for a direct comparison of intensities between the two panels. Remarkably, the effects of applying a 7.5 T field and disordered oxygen lattice are nearly identical. A field of 5 Tesla reduces \( T_c \) in our sample by \( \sim 10 \text{ K} \) and, as reported above, increasing the degree of dopant disorder reduces \( T_c \) by about 5 K. These reductions in \( T_c \) are comparable, as are the enhancements of the SDW intensity. In the generalized Landau theory of Demler et al., the superconducting order parameter and the SDW order parameter are repulsively coupled and coexist at the microscopic level. By suppressing the superconducting order parameter, the magnitude of the SDW order parameter should increase, which is consistent with the totality of our observations.

The exact mechanism leading to the enhanced \( T_c \) in the ordered-oxygen state is unclear. Oxygen ordering has also been observed to enhance superconductivity in other cuprate superconductors, such as YBa\(_2\)Cu\(_{3}\)O\(_{6+x}\) [14] and Tl\(_2\)Ba\(_2\)CuO\(_{6+\delta}\) [15]. For these materials, this enhancement results at least in part from charge transfer to the CuO\(_2\) planes caused by changes in the valence of cations in other layers (such as Cu\(^{1+}/2^+\) in the chain layers of YBa\(_2\)Cu\(_3\)O\(_{6+x}\)). Such a mechanism cannot explain the effect in La\(_2\)CuO\(_{4+y}\) which does not have multivalent cations outside of the CuO\(_2\) layers. Hence, the enhanced \( T_c \) is almost certainly related to the ordering of the oxygen intercalants. We note that macroscopic phase separation does not occur in stage-4 La\(_2\)CuO\(_{4+y}\), and that the hole density is as uniform as that in La\(_{2-\delta}\)Sr\(_x\)CuO\(_4\) with \( x \approx 0.14 \). As discussed in our previous work, the scaling of \( \chi(T) \) and the \(^{63}\text{Cu} \) NQR frequency and \( 1/T_1 \) behavior in our crystals with \( T_c \sim 42 \text{ K} \) are consistent with a single hole concentration [3, 4]. In samples with lower oxygen concentrations (with \( T_c \approx 32 \)), it has been well documented that rapid quenching from room temperature to below \( T_c \) on the time scale of a few tens of seconds, can reduce the superconducting \( T_c \) compared to that attained on slow cooling. As mentioned above, we have found that a stage-6 crystal also possesses an ordered oxygen lattice at low temperatures (which becomes disordered above \( \sim 210 \text{ K} \)), and it is likely that destruction of the oxygen order is responsible for the shift in \( T_c \).

In summary, we have found that the staging behavior observed in La\(_2\)CuO\(_{4+y}\) is associated with a three-dimensional ordering of the excess oxygen dopants. Our results indicate that the high \( T_c \) of stage-4 La\(_2\)CuO\(_{4+y}\) is correlated with the ordering of the oxygen dopants. Increasing the degree of disorder enhances the SDW order parameter in a manner similar to the effect of applying modest magnetic fields. These results further support the idea that superconductivity and SDW order coexist and compete.

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