Charge and Spin Structure in $YBa_2Cu_3O_{6.35}$

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Neutron scattering has been used to measure the charge and spin structure in the highly underdoped superconductor $YBa_2Cu_3O_{6.35}$. Incommensurate static charge ordering is found that remains at high temperatures. The magnetic pattern is complex with a resonance and incommensurate structure observed at low temperatures. The results clarify the role of striped phases in $YBa_2Cu_3O_{6+x}$ superconductors.

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Despite the vast amount of work on the cuprate materials there is still little agreement on the origin of the superconductivity. From the beginning it was understood that the cuprates display very unusual properties and a number of ideas have emerged in effort to understand them. One fascinating concept is that spin and charge separate into different linear regions or stripes [1–6] in the material. Neutron scattering measurements have observed a pattern of incommensurate spin fluctuations in the $La_xSr_{1-x}CuO_4$ (LSCO) [7] and $YBa_2Cu_3O_{6+x}$ (denoted as YBCO6 + x) [8] superconductors consistent with the stripe picture. These peaks were observed around the magnetic superlattice positions of the basic antiferromagnetic (AF) spin structure. The position is the (π, π) point in square lattice notation. However, the key issue for the stripe picture is the presence of the charge distribution. Indeed, it is the charge that first organizes itself into the shape that determines the stripe structure and the spins arrange themselves to fit this structure as the temperature is lowered. The first experiments to see both the charge and spin structures were done by Tranquada and co-workers [9] on a LSCO material in which Nd was added which froze the normally moving spins and charges into a static structure. The charge distribution cannot be seen directly by neutrons, but only indirectly by the atoms that move in response to the charge. The response of the atoms is found by observing peaks surrounding the reciprocal lattice positions of the crystal lattice. In an ideal picture, the signature of a striped phase is that the wave vector of the charge peaks is twice that of the spin peaks. This is caused by an antiphase spin boundary at the charge stripe resulting in a spin repeat unit cell twice that of the charge unit cell.

A major advance in the present experiments is that static charge order has been observed in the (YBCO)6 + x materials for the first time. In fact, the charge ordering occurs directly within the YBCO6 + x phase without the need for additions like Nd. The charge order has been observed in (YBCO)6.35 which is a superconductor with a transition temperature T_c of about 39 K as determined from the midpoint of a transition that is about 10 K wide. Such broad transitions are often seen in the large melt-grown heavily underdoped materials used in the experiments, which may mean that the materials are disordered in some way. However, the charge response peaks are very narrow. The material is orthorhombic with sharply defined lattice constants of $a = 3.8438 \pm 0.0005$ Å, $b = 3.8708 \pm 0.0005$ Å, and $c = 11.801 \pm 0.001$ Å. The YBCO6.35 composition may be found to have a different T_c or be AF by other groups; however, this may depend on how the oxygenation takes place. The material is best characterized by the lattice constants and T_c value. The crystal weighs 21.07 g and has a mosaic spread of 1°.

It is very difficult to detect static charge order, as a large elastic background is present from spin and isotopic incoherent processes. Even more bothersome is the fact that the large crystal sample used in the measurements contains other phases such as Y_2BaCuO_5 in the form of powders. Powder lines from these phases obscure the small peaks stemming from charge order. Charge scattering was searched for around the Bragg reflections of the lattice along the $a^*(b^*)$ direction for various values of c^*. The crystal used in the experiments is twinned so that a^* could not be distinguished from b^* in the measurements. The measurements were made on the triple-axis spectrometers at the high-flux isotope reactor (HFIR) at Oak Ridge National Laboratory. Collimation was 48′-20′-20′-60′ from before the monochromator until after the analyzer. Pyrolytic graphite with a 30′ mosaic spread was used for the monochromator and analyzer crystals. The neutron incident energy was 13.7 meV giving an energy resolution of about 0.75 meV. Pyrolytic graphite filters were used in the beam to avoid higher order contamination from the monochromator and analyzer crystals. The momentum transfer $q = (q_x, q_y, q_z)$ in units of Å^{-1} is the position $(h, k, l) = (q_x a/2\pi, q_y b/2\pi, q_z c/2\pi)$ in reciprocal lattice units (r.l.u.).

A large number of scans were made at various positions in the reciprocal lattice to search for charge order. Since charge order is not observed directly but from atomic displacements, it is not immediately obvious which reciprocal lattice positions should yield the largest signal. The scans in Fig. 1 show the two places in the reciprocal lattice where clean data could be obtained. The first of these is near the origin of reciprocal space where there are no competing

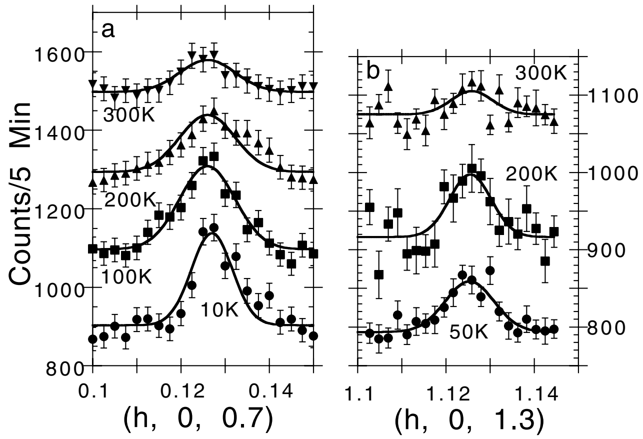

FIG. 1. Measurements of the charge order for YBCO6.35. (a) Measurements obtained at a small momentum transfer so the results are not affected by impurity powder lines. Powder lines were also avoided around the $(1.125, 0, 1.3)$ r.l.u. position shown in (b). The lines are Gaussian fits to the data. In (a) 200 and (b) 100 additional counts were added onto successive scans so the data could be presented on the same plot. The scattering broadens at higher temperatures.

powder lines. This is not a typical place to search for charge order as charge scattering usually gets less intense as the momentum transfer q is reduced. However, resolution effects reduce the peak heights at larger q while the large Debye-Waller factor for oxygen further decreases the intensity. It also happens that the composition studied results in a charge order that is essentially commensurate, having a period of eight lattice units. This may serve to enhance its visibility. Scans near $(1.125, 0, 1.3)$ r.l.u. also gave clean results.

The data in Figs. 1a and 1b have been normalized to a 5 min counting time. Multiple runs were averaged together resulting in the counting errors shown. The peaks are small, being about 10^{-6} of the strongest crystal Bragg peaks. The charge order occurs at 0.127 ± 0.002 r.l.u. along $a^*(b^*)$. The 10 K peak is narrow with a resolution limited width of about 0.011 ± 0.002 r.l.u. FWHM. This results in a minimum correlation length of $\sim$350 Å in the $a^*(b^*)$ direction. The data in both Figs. 1a and 1b show the same behavior. The charge peaks decrease in intensity as the temperature is increased, but are still visible at 300 K which is the highest temperature of the measurement. Measurements were also made for YBCO6.5 and for YBCO6.6, but no static charge order could be found.

Since the peaks are too small for polarization analysis we cannot rule out the possibility that the peaks are some kind of unexpected magnetic order. However, this seems very unlikely as the peaks are found around the crystal lattice positions rather than the magnetic positions. Furthermore, it should be noted that the peaks occur at exactly the point of maximum broadening of the $\langle B_{2u}, B_{3u}\rangle$ phonon discussed in Ref. [10]. The broadening of the phonon results from fluctuations of the charge order. This now establishes a direct link between the phonon anomalies and charge order so that when the charge order vanishes at higher doping levels the charge fluctuations can still be followed through the phonons. This also gives us confidence that the elastic peaks we observe correspond to charge order. No peaks are expected from oxygen order in the chains at the wave vector of the observed scattering [11].

We now consider measurements of the magnetic structure. In this case detailed measurements as a function of energy can be made since there is a direct interaction between the neutron spin and the electronic spins. To cover a large energy range with good resolution, a number of spectrometer configurations were used. In general the final neutron energy was 13.7 meV and a graphite filter was used to remove higher order contamination. A pyrolytic graphite monochromator was typically used for energy transfers below 20 meV, while a Be monochromator was used for higher energy transfers to obtain sufficient resolution. When the spectrometer configuration was changed, overlapping data sets were taken so that all measurements could be normalized on the same scale.

The measurements to examine the magnetic excitations were made around the AF position $(0.5, 0.5, 5.2)$. For severely underdoped superconducting YBCO6 + x, a broad commensurate peak is observed at low energy transfers. For YBCO6.45, scans at 10 meV showed a broad commensurate peak while incommensurate scattering is observed at higher energy transfers [12]. For YBCO6.35, measurements of the magnetic scattering are shown in Fig. 2. At 4 and 8 meV, we observe only commensurate peaks centered around (π, π). For a 15 meV energy transfer, incommensurate peaks appear in addition to the central distribution as shown in Fig. 2c. These peaks vanish when the temperature is raised to 100 K as shown in Fig. 2d. A scan taken at 200 K looks identical to the scan in Fig. 2d if the temperature population factor is taken into account. This means that the spin susceptibility for the broad commensurate peak has a different temperature scale than the incommensurate excitations. Figure 2e shows that at energies near 25 meV the scattering is found closer to the commensurate position. Figure 2f gives the 25 meV scattering at 100 K. The 100 K distribution is less peaked at the commensurate position resulting in the resonance excitation appearing at low temperatures. Figure 2g gives an energy scan at (π, π) showing the difference between the intensity at 10 and 60 K. This is the typical signature of the resonance. At energy transfers above the resonance evidence for incommensurate peaks on the sides of the central distribution are again observed as shown in Fig. 2h.

The usual way to examine the low temperature magnetic excitations is to subtract high temperature data corrected for the Bose population factor from data obtained at low temperatures [12,13]. Accordingly we made a series of scans at different energy transfers at both 10 and 100 K. The scans were typically made at 2 meV intervals below 30 meV and at 2.5 meV intervals above 30 meV. Figure 3 shows the result of the subtracted measurements. Below

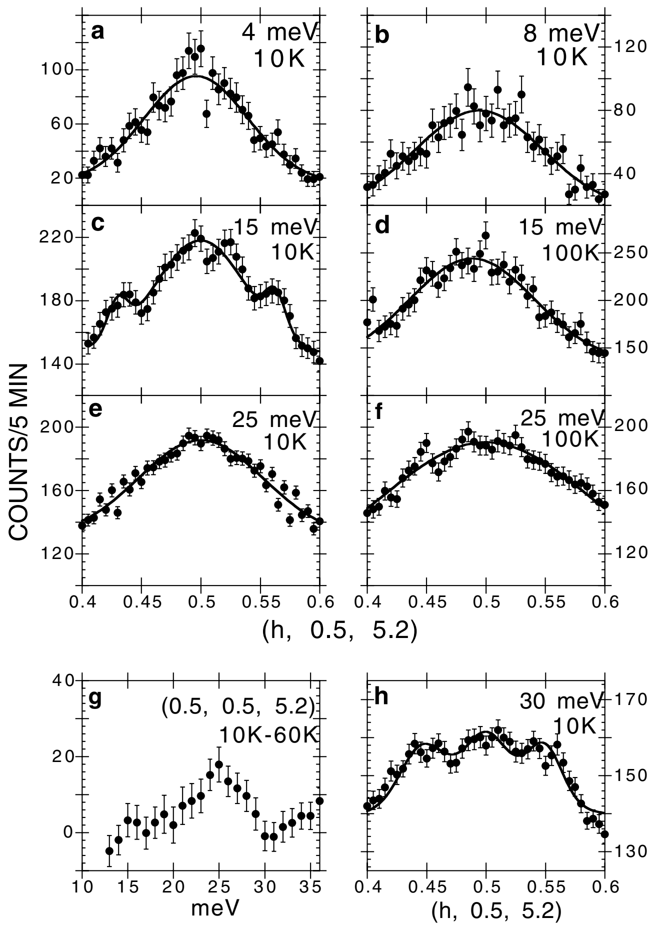

FIG. 2. Measurements of the magnetic fluctuations for YBCO6.35. (a) and (b) Show that only a broad commensurate peak is found at low energies. Here the line is a Gaussian fit to the data. (c) Demonstrates that at 15 meV incommensurate peaks are found on either side of a commensurate distribution. The solid line is a fit of three Gaussians to the data. (d) Gives measurements at 15 meV for 100 K showing that the incommensurate peaks have disappeared at the higher temperature. (e) and (f) Display results near the resonance energy. The lines are the fit of a single Gaussian peak. (g) Gives the difference of energy scans at (π, π) for 10 and 60 K taken to observe the resonance. (h) Shows results at 30 meV where the line is a fit of three Gaussian peaks. The error bars result from averaging a number of scans.

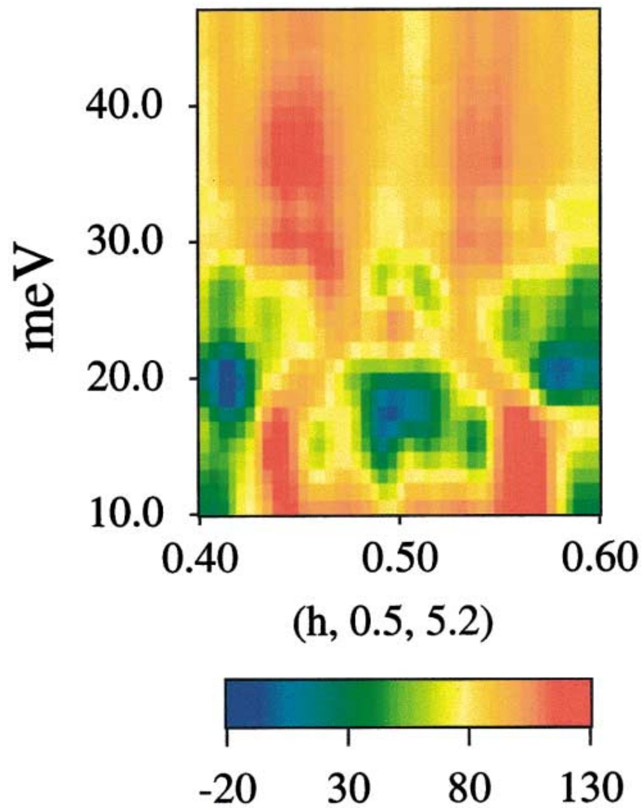

FIG. 3 (color). Magnetic scattering distribution for YBCO6.35 obtained by subtracting 100 K data from data taken at 10 K. The small resonance can be observed at (0.5, 0.5, 5.2) and 23 meV. The intense incommensurate scattering between 12 and 17 meV is at the right wave vector for charge and spin scattering to result from a striped phase.

10 meV no incommensurate peaks were visible, only a distribution centered at the commensurate position. At energies from about 12 to 17 meV incommensurate peaks were found at about 0.0625 r.l.u. from the commensurate (0.5, 0.5, 5.2) position. This is $1/16$ r.l.u., so in this energy region there are magnetic peaks corresponding to the stripe phase spacing of the charge distribution which is $1/8$. We note there is a gap of about 10 meV where no incommensurate magnetic excitations are observed so that there is no static striped phase. Above 17 meV the wave vector of the incommensurate scattering decreases as the resonance energy of about 23 meV is approached. This behavior [12–14] has been observed previously for higher hole doping, but in these cases the resonance is much more intense than the incommensurate scattering. In this case the resonance scattering is small so that the incommensurate scattering is easier to follow in the region of the resonance. It appears that both the incommensurate fluctuations and the resonance are observed separately at the resonance energy. However, the data are not sufficiently accurate to determine this, and scans made near the resonance energy show no convincing evidence of peaks from both the resonance and the incommensurate scattering.

Since it has been known that for YBCO6 + x the spacing of the incommensurate peaks varies as a function of energy, the obvious question has been to what extent the peaks can be thought of as stemming from a striped phase. The spacing of the charge fluctuations has been measured in the present case so that this question can be addressed. Only the lowest energy magnetic incommensurate scattering has the correct spacing of $1/16$ r.l.u. to result from antiphase boundaries at the charge stripe. Above 17 meV the resonance and the incommensurate fluctuations may be connected in some way. There are a number of different theories for the origin of the resonance. We cannot consider them here, but they are discussed in Ref. [12]. It should be noted that the resonance is barely visible in a material with a T_c near 35 K. That may explain why the resonance has not been found in the LSCO materials.

By observing both the spin and charge fluctuations in the low doping material, we can speculate on the role played by striped phases as the hole-doping level increases. Measurements of the incommensurate spin fluctuations have now been made for hole doping up to the optimal value [12]. We first consider YBCO6.6 which has a hole doping of 0.1. The magnetic excitations can be pictured by shifting the whole pattern in Fig. 3 up in energy so the resonance energy is at 34 meV. In addition, the superconducting gap cuts off more of the lower energy scattering while the incommensurate wave vector increases to $1/10$ r.l.u. for the lowest energy excitations. Measurements of the lowest energy spin fluctuations show that they are one-dimensional [15] as expected for a striped phase. However, now the range in energy for which low energy scattering is at a constant spacing is reduced compared to YBCO6.35. At the optimal doping level of YBCO6.93 with a hole content of about 0.15 the magnetic pattern is shifted upwards so that the resonance is at 41 meV. However, the gap in the magnetic spectrum has increased, cutting more off the low energy part of the magnetic spectrum. This leaves little if any magnetic incommensurate scattering that is at a constant spacing over any appreciable energy range. Thus as doping is increased magnetic scattering that can be associated with antiphase stripe boundaries reduces. It is also interesting to note that in YBCO6.35 and YBCO6.6, where the incommensurate peaks are best defined, the stripe spacing is nearly a multiple of the lattice spacing. This may mean that the lattice helps to stabilize stripes.

Our results provide the first observation of charge order in the YBCO6 $+ x$ materials. It seems that even static charge order is compatible with superconductivity as long as spin order remains dynamic. This agrees with results by Ichikawa *et al.* [16] on $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$. Measurements of the magnetic fluctuations show that only the lowest energy excitations have the right spacing to be associated with a striped phase. It is not clear how this affects the idea of a 1D-phase separation [17] that promotes superconductivity.

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